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TANNING MATERIAL

Alfred Russell and John W. Copenhaver, Philadelphia, Pa., assignors to Röhm & Haas Company, Philadelphia, Pa.

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This invention relates to an improvement in tanning materials made by condensing naphthalene sulfonic acids with formaldehyde.

It is known that the condensation products of naphthalene sulfonic acid and formaldehyde have valuable tanning properties. They have been used extensively in tanning pickled stock, in brightening chrome tanned leather, and in retanning leather already tanned by other tanning materials. They produce, however, when applied to pickled stock, a leather which is drawn and stiff and lacking entirely the fine soft flexibility of well-tanned leather.

The object of this invention is to improve the tanning qualities of the naphthalene sulfonic acid-formaldehyde condensation products, both when used as the primary tanning material and when used as a retannage to leather already made by other means. A further object is to improve the bleaching properties of the same condensation products when applied to chrome leather. A still further object is to improve the tanning qualities of those condensation products so that soft, flexible leather is obtained that is white in color and similar to vegetable tanned leather in quality.

These objects we have accomplished through our discovery that certain relatively water insoluble phenolic compounds, notably dihydroxy diaryl compounds, when merely dissolved in an aqueous solution of a naphthalene sulfonic acid-formaldehyde condensate materially improve the tanning qualities of those condensates. The phenolic compounds useful for this purpose are those non-resinous phenols which are normally considered water insoluble or only slightly water soluble. Among these are aryl substituted phenols, such as p-phenyl phenol; and dihydroxydiaryl compounds, such as those in which the aryl groups are connected by a carbon or sulfur bridge. Among the latter may be mentioned 4,4'-dihydroxy-diphenyl dimethylmethane, dihydroxyditolyl dimethylmethane, 4,4'-dihydroxy diphenylsulfone, 4,4'-dihydroxy ditolylsulfide, 4,4'-dihydroxy diphenylsulfide, 4,4'-dihydroxy diphenylmethane, and the dihydroxyditolyl methanes.

In practicing the invention the phenolic compound is merely dissolved in the aqueous solution of the naphthalene sulfonic acid-formaldehyde condensation product, preferably by stirring the mixture and slightly heating. Raising the temperature is not however, necessary but substantially hastens the rate at which the phenolic compound dissolves. The concentration of condensation product in the aqueous solution also affects the rate of solution, the phenolic compounds being more readily soluble in the more concentrated solutions. For this reason it is desirable to dissolve the phenolic compound in a concentrated solution of condensation product

and after solution is complete, diluting to the appropriate concentration. For maximum improvement in tanning properties the solution should be nearly saturated with the phenolic compound. A suitable safety factor to prevent changes in temperature resulting in precipitation of phenol should be allowed. If less phenolic compound is used a greater amount of tanning agent is needed to produce the same quality leather.

In the following examples given to illustrate how the invention is carried out definite temperatures and concentrations are specified. It should be understood that these and other details are those that may conveniently be used and that the invention is not limited to them.

Example 1.—125 grams of the strongly acid condensate obtained by condensing naphthalene sulphonic acid with formaldehyde in acid solution is dissolved in 250 grams of water and the solution stirred and heated to 60° C. 14 grams 4,4'-dihydroxy diphenyl dimethylmethane is added and the whole stirred and heated to approximately 60° C. for approximately forty minutes or until solution is complete. The solution is then cooled, treated with approximately 10 grams sodium hydroxide to reduce the acidity of the final solution to the equivalent of approximately 3.6% sulphuric acid by volume and diluted with water to a final volume of 450 cc. The solution so prepared may be used directly for tanning pickled stock, for retanning leather already made by other means, and for brightening or bleaching chrome leather.

Example 2.—125 grams of the strongly acid condensate obtained by condensing naphthalene sulphonic acid with formaldehyde in acid solution is dissolved in 250 grams of water and the whole made faintly alkaline by the cautious addition of soda ash. The solution is filtered and in the filtrate 2.5 grams of caustic soda dissolved. 12.5 grams 4,4'-dihydroxy diphenyldimethylmethane is then added and the mixture stirred and heated at 50–60° C. until solution is complete. The solution is cooled, reacidified with sulphuric acid so that the acidity of the final solution is equivalent to approximately 3.6% sulphuric acid by volume (approximately 21.6 grams sulphuric acid being required) and diluted with water to 450 cc. The product so obtained is very similar to that described in Example 1 and may be used for the same purposes.

Example 3.—A water solution of the condensation product of naphthalene sulphonic acid and formaldehyde is prepared as in Example 1 and in the water solution 15 grams of 4,4'-dihydroxy diphenyl sulphone is dissolved. The solution is cooled, neutralized and diluted as is the solution in Example 1. It may be used for the same purposes.

Example 4.—An alkaline solution of the condensation product of naphthalene sulphonic acid and formaldehyde is prepared as in Example 2. In this solution 12.5 grams of 4,4'-dihydroxy diphenylsulphone is dissolved and the solution cooled, acidified and diluted as in Example 2.

Instead of dissolving a single phenolic compound in the naphthalene sulphonic acid-formaldehyde condensate more than one may be added. Examples 5 and 6 illustrate the use of both the phenolic compounds employed in the preceding examples.

Example 5.—400 grams of the final solution prepared according to the procedure described in Examples 1 and 2 is heated to 50–60° C. and 9 grams of 4,4'-dihydroxy diphenyl sulphone added. The new solution obtained is cooled and water added to compensate for any loss by evaporation. It may be used directly for the same purpose as described in Example 1.

Example 6.—An alkaline solution of the condensation product of naphthalene sulphonic acid and formaldehyde is prepared as described in Example 2 using the same quantities. This solution is heated to 50–60° C. and 12.5 grams 4,4'-dihydroxy diphenyl dimethylmethane and 10 grams of 4,4'-dihydroxy diphenyl sulphone dissolved therein by stirring. The solution is cooled, acidified and diluted as in Example 2.

Tanning solutions similar to those prepared in Examples 1 and 2 that may be used for the same purposes, can be made by substituting for the dihydroxy diphenyl dimethyl methane, equivalent quantities of 4,4'-dihydroxy diphenyl methane or 4,4'-dihydroxy ditolyl methane, prepared by condensing two molecular equivalents of phenol or cresol with one molecular equivalent of formaldehyde. In the alternative these phenolic compounds can be formed in situ as by the following procedure.

Example 7.—125 grams of the strongly acid condensate obtained by condensing naphthalene sulphonic acid with formaldehyde is dissolved in 62.5 grams of water. In this solution 47 grams of phenol or an equivalent amount of cresol is dissolved. The solution is cooled to 0° C. and 19 cc. of 37% aqueous formaldehyde added dropwise over ten minutes. The whole is stirred six hours at 0° C. or until the odor of phenol or cresol has disappeared. The solution is now treated with 10 grams caustic soda and diluted with water to 450 cc. After any insoluble matter is removed by filtration the solution may be used for the same purposes as described in Example 1.

By substituting for the phenolic compounds in these examples, particularly in Examples 1 and 2, any of the other phenolic compounds herein mentioned, such as p-phenyl phenol, 4,4'-dihydroxy ditolyl sulphide, 4,4'-dihydroxy ditolyl dimethyl methane, analogous tanning materials useful for the same purposes may be made. While improved tanning qualities are obtainable with any of the phenols having only slight solubility in pure water, we have found the dihydroxy diphenyl compounds of the benzene series, particularly those in which the phenyl groups are joined to a carbon or sulphur bridge, give the best results. The procedure by which these improved tanning materials are used in preparing leather is the same as is now employed using unmodified naphthalene sulfonic acid-formaldehyde condensates.

We claim:

1. As an improved tanning material as aqueous solution of a naphthalene sulphonic acid-formal-

dehyde condensation product having dissolved therein a dihydroxy diphenyl dimethyl methane and a dihydroxy diphenyl sulphone.

2. As an improved tanning material an aqueous solution of a naphthalene sulphonic acid-formaldehyde condensation product having dissolved therein a dihydroxy diphenyl dimethyl methane.

3. As an improved tanning material an aqueous solution of a naphthalene sulphonic acid-formaldehyde condensation product having dissolved therein a dihydroxy diphenyl sulphone.

4. As an improved tanning material an aqueous solution of a naphthalene sulphonic acid-formaldehyde condensation product nearly saturated with a dihydroxy diphenyl dimethyl methane and a dihydroxy diphenyl sulphone.

5. As an improved tanning material an aqueous solution of a naphthalene sulphonic acid-formaldehyde condensation product nearly saturated with a dihydroxy diphenyl dimethyl methane.

6. As an improved tanning material an aqueous solution of a naphthalene sulphonic acid-formaldehyde condensation product nearly saturated with a dihydroxy diphenyl sulphone.

7. An improvement in the tanning of leather with naphthalene sulphonic acid-formaldehyde condensation products which consists in incorporating in the solution of the tanning agent a dihydroxy diphenyl dimethyl methane and a dihydroxy diphenyl sulphone.

8. An improvement in the tanning of leather with naphthalene sulphonic acid-formaldehyde condensation products which consists in incorporating in the solution of the tanning agent a dihydroxy diphenyl dimethyl methane.

9. An improvement in the tanning of leather with naphthalene sulphonic acid-formaldehyde condensation products which consists in incorporating in the solution of the tanning agent a dihydroxy diphenyl sulphone.

10. The process of preparing an improved tanning material which comprises condensing naphthalene sulfonic acid with formaldehyde in acid solution and dissolving therein dihydroxy diphenyl sulfone.

11. The process of preparing an improved tanning material which comprises condensing naphthalene sulfonic acid with formaldehyde in acid solution, and dissolving in said solution a dihydroxy diphenyl methane and a dihydroxy diphenyl sulfone.

12. As an improved tanning material an aqueous solution of a naphthalene sulfonic acid-formaldehyde condensation product having dissolved therein a member of the group consisting of dihydroxy diphenyl dimethyl methane, dihydroxy diphenyl sulfone and mixtures thereof.

13. The process of preparing an improved tanning material which comprises condensing naphthalene sulfonic acid with formaldehyde in acid solution and dissolving therein a member of the group consisting of dihydroxy diphenyl dimethyl methane, dihydroxy diphenyl sulfone and mixtures thereof.

14. An improvement in the tanning of leather with naphthalene sulfonic acid-formaldehyde condensation product which consists in incorporating in the solution of the tanning agent a member of the group consisting of dihydroxy diphenyl dimethyl methane, dihydroxy diphenyl sulfone and mixtures thereof.

ALFRED RUSSELL,
JOHN W. COPENHAVER.