

UNITED STATES PATENT OFFICE

2,136,997

TANNING AGENTS

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No Drawing. Application February 10, 1937, Serial No. 125,154. In Germany February 14, 1936

8 Claims. (CL. 149—5)

The present invention relates to tanning agents. In U. S. application Serial No. 123,734, filed February 2, 1937, by Arthur Voss, Walter Pense, Heinrich Janz and Werner Asch entitled "Tanning agents and a process of preparing them" a process of preparing water soluble derivatives of natural resins is described which comprises treating mixtures of resin and phenols or the resin-esters obtainable by heating such mixtures with sulfonating agents and eliminating the sulfonation products to a far extent from the adhering electrolytes. By this process these resin-sulfonic acids which as such are very sensitive to electrolytes and therefore are not very suitable as tanning agents become valuable tanning agents. It is possible completely to remove the electrolytes but under industrial conditions this is very difficult. On the other hand, if all the electrolytes are not removed, there is a certain difficulty in dissolving the product and that is sometimes detrimental.

We have found that a profound insensibility to electrolytes still present may be attained by mixing the products obtained by sulfonating mixtures of resins and phenolic bodies or the esters thereof with synthetically prepared tanning agents. As such tanning agents there may especially be mentioned all sulfonic acids of compounds of high molecular weight obtained by linking several aromatic nuclei, i. e. the sulfonic acids of condensation products obtained from aromatic bodies (phenols, naphthalene, aniline etc.) and bridge-forming agents, such as aldehydes, sulfur, sulfur chloride. In this case the sulfo group may be introduced either directly or by esterification, peptisation etc.

In combination with the products described in the copending application mentioned above the known synthetic tanning agents are far less sensitive to the action of electrolytes. Furthermore the properties of these new mixtures may be varied to a greater extent than those of the known synthetic tanning agents. The mixtures may, therefore, be successfully applied in far more tanning processes of various kind than the known synthetic tanning agents.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto; the parts are by weight:—

(1) 100 parts of a resin-sulfonation product obtainable from pine resin and phenol prepared according to the afore-named U. S. application Serial No. 123,734 are dissolved in 200 parts of water at a temperature of 50° C. The solution is mixed with 100 parts of a tanning agent ob-

tained by sulfonating 81.5 parts of alpha-methyl naphthalene with 110 parts of sulfuric acid (of 100 per cent. strength) and by peptizing into this solution 70 parts of a liquid resin made by alkaline condensation of two mols of phenol with 1 mol of paraformaldehyde. The solution is stirred at 50° C. until it has completely become homogeneous and is brought to a pH-value of nearly 3 by the addition of caustic soda solution. Thereby the sensitivity to salt of the solution is diminished to a great extent. Calf pelts are tanned with this combination by treating them in a pit with liquors beginning with a strength of 0.5° Bé. A leather is thus obtained showing a light color and having smooth grains and a very good stretch.

(2) 400 parts of resinic ester prepared by esterification up to the acid number 20 of American colophony with tricresol are sulfonated with fuming sulfuric acid of 10 per cent. strength; as described in U. S. application Serial No. 123,734 the mixture is freed from electrolytes by washing it out, drying and grinding it. 200 parts of this powder are gradually added to 500 parts of a solution of tanning agents of 25 per cent. 25 strength prepared—similarly to Example 1—by peptizing a phenol-formaldehyde resin into butyl-naphthalene sulfonic acid. With this tanning agent cow pelts are tanned in a drum. The strength of the liquors begins with 1° Bé. and is increased during the tannage up to 5° Bé.

(3) 120 parts of the resin-sulfonic acid prepared according to Example 5 of U. S. application Serial No. 123,734 from 120 parts of liquid Swedish resin and 46 parts of beta-naphthol are dissolved in 200 parts of water and the solution is rendered distinctly acid with formic acid. 50 parts of a synthetic tanning sulfonic acid obtained by causing formaldehyde to react upon naphthalene sulfonic acid are stirred into the solution. The homogeneous solution is evaporated so as to form a dry substance which is pulverized. A mixture of, for instance, 50 parts of quebracho (soluble in the cold state, solid) and 50 parts of the powdered tanning agent described above is dissolved in water so as to form a liquor of a strength of 10° Bé. In this liquor cow pelts are tanned which already have been tanned through in the color pits. When being treated with this combination the leather obtained is of lighter color and a better stretch and is more plump than that treated with quebracho alone.

We claim:

1. A tanning agent consisting of the sulfonation product from a mixture of a phenolic body

and a natural resin and having a content of an electrolyte not higher than 10 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 5

2. A tanning agent consisting of the sulfonation product from phenolic bodies and natural resins, esterified in the presence of catalysts, with a content of electrolyte not higher than 10 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 10

3. A tanning agent consisting of the sulfonation product from a mixture of colophony and phenol and having a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 15

4. A tanning agent consisting of the sulfonation product from equimolecular proportions of colophony and phenol with a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 20

5. A tanning agent consisting of the sulfonation product from colophony and cresol and having a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 25

6. A tanning agent consisting of the sulfonation product from equimolecular proportions of colophony and cresol and having a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 30

7. A tanning agent consisting of the sulfonation product from colophony and xyleneol and having a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 35

8. A tanning agent consisting of the sulfonation product from equimolecular proportions of colophony and xyleneol with a content of electrolyte not higher than 10 per cent., calculated upon a tanning agent of 100 per cent., mixed with synthetic tanning agents of the group consisting of water soluble polynuclear aromatic condensation products. 40

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