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# UNITED STATES PATENT OFFICE

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## COLLOIDAL SUSPENSION AND METHOD OF USE

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This invention relates to a new process of treating hides or skins.

The process of tanning as generally understood consists in the treatment of hides or skins with aqueous solutions of materials which will interact with the hide substance to produce compounds insoluble in water. These materials generally form colloidal solutions. They vary widely in composition, the main classes, however, consisting of (1) the natural vegetable tannings, (2) suitable mineral salts, such as those of chrome or alum, (3) snythetically prepared organic materials. Each of these classes give leather with certain advantages and disadvantages. For example, the impregnation of heavier hides with natural tannins has necessarily to be carried out slowly, and the resulting leather is not resistant to water at high temperatures. On the other hand chrome tanning is a rapid process, and the leather obtained withstands the action of hot water, but it is somewhat lacking in weight and fullness. In order to secure the best results a combination of two or more of these classes of tanning materials is frequently used. By admixture of synthetic organic products of suitable type the process of tanning with the natural vegetable tannins can be speeded up. In the case of chrome tannage, the lack of fullness is frequently corrected for by a supplementary tannage with natural tannins. But the amount of such a supplementary tannage is limited, since there is a tendency to weaken the grain and render it harsh.

I have now discovered a new class of synthetic organic materials which give a more rapid tannage when blended with natural vegetable tannins, and which are specially useful when used as a supplement to chrome tanning, since they give a decided increase in fullness and weight to the leather, without rendering the grain harsh, and even strengthen instead of weakening it when used in large amounts.

The new process of tanning, briefly, consists in the application to the skin of a colloidal suspension of a resinous product, which is deposited on the fibres of the skin, and imparts weight and fullness without causing weakening of the grain.

It is somewhat difficult to prepare such suspensions but by dispersion of the resin in situ at the moment of its formation I have found it possible to manufacture a standard product, which has been utilized in tanning with consistently good results. The actual details of preparation are illustrated in the examples below, but the general method is to take a sulphonic acid containing a naphthalene or substituted naphthalene nucleus, and react on it in presence of formaldehyde with naphthalene or one of its derivatives, using sulphuric acid as condensing agent. In this way the resin is dispersed as it is formed, in the sulphonic acid solution. Any excess of sulphuric acid present is then neutralized with soda, the solution diluted to standard strength and used directly in tanning. It may readily be shown that a resin is present since on extraction with benzene the white suspension breaks down, and on evaporation of the benzene the resin is obtained in free state. It can not be redispersed in the aqueous extract once the suspension has been broken. This is an important factor in the utilization of such materials in tanning.

The tanning process with such colloidal suspensions is capable of wide variations to suit the nature of the skin treated, and the tannage customarily used. On leather normally tanned with the natural tannins, it is best to use a blend of the new product with the natural tannins. On mineral tanned leather it is best to complete the tannage with mineral salts and then apply the new product as a retannage. In some cases it is advantageous to tan with chrome and give as a retannage a blend of natural vegetable tannins and the new product.

While these new materials are of primary interest in the leather field, they have also been found useful as dispersing agents and wetting agents, and in imparting weight to textile fibres.

The following examples illustrate the method of preparation of these new products and their utilization in the treating of

hides and skins, but the invention is in no way restricted to these examples:

*Example 1*

A colloidal suspension is prepared as follows:

A mixture of
640 grams naphthalene
640 grams sulphuric acid 98%
is heated to 130° C. for 6 hours, then cooled to 100° C.

Then
1540 grams dibenzylnaphthalene
700 grams sulphuric acid 70%, are added. Temperature is adjusted to 85° C. and 520 grams formaldehyde 37% are run in over a period of 2 hours, while the mixture is well stirred. Stirring is continued at 85–90° C. for 4 hours. The mixture is then diluted with 900 c. c. water and the excess of mineral acid neutralized with caustic soda, given in concentrated solution. The product is diluted to 5750 grams. In this way a creamy liquid is produced which disperses readily in water.

100 lbs. of pickled sheepskins are placed in a drum with 250 lbs. of 5% salt solution and the drum set in motion. 50 lbs. of a blend of 3 parts liquid quebracho extract and 1 part of the above product is added in four feeds at 1 hour intervals. The skins are allowed to lie in the liquor overnight, then thoroughly washed out and finished up as usual.

*Example 2*

A colloidal suspension is prepared as follows:

A mixture of
640 grams naphthalene
640 grams sulphuric acid 98%
is heated to 130° C. for 6 hours, then cooled to 40° C.

640 grams naphthalene
5300 grams sulphuric acid 50%
650 grams formaldehyde 37%, are added.

Mixture is heated up in an open container to 90° C. and stirred at 90–95° C. for 5 hours.

During the last two hours some separation of solid occurs. On cooling a solid separates on the surface, from which the clear acid layer below is removed, the solid washed several times with water and dried. It is then dissolved in water, the occluded free sulphuric acid neutralized with caustic soda, and the solution diluted to 16 kilograms.

In a regular process of yard tannage of heavy hides the above solution is added to the tail liquor of the yard, using 2 lbs. per hide. The resulting leather is better filled than when no colloidal suspension is present, and the rate of tanning is increased.

*Example 3*

100 lbs. kidskins which have been chrome-tanned by the two bath process but not finally neutralized are placed in a drum with 300 lbs. water at 80° F. and treated with 15 lbs. of the product prepared as in Example 1. The drum is rotated for 1 hour, then the skins are thoroughly washed, neutralized and finished up as usual.

*Example 4*

A colloidal suspension is prepared as follows:

66 grams tetralin
144 grams sulphuric acid 98%
are heated at 100° C. for 6 hours, when a completely soluble product is obtained. Mixture is cooled somewhat, and
20 cc. water added, followed by
64 grams naphthalene.

Mixture is heated to 85° C. and 54 grams formaldehyde 37% added in course of 2 hours.

Mixture is stirred for 4 hours at 85–90° C., then diluted with water and the excess of sulphuric acid neutralized with caustic soda. Solution is diluted to 575 grams.

A sheepskin which has been chrome-tanned and shaved, but not neutralized, and weighs about 2 lbs. is placed in a small drum with 6 lbs. water at 80° F. and ¼ lb. of product prepared as above added. The drum is rotated for 1 hour, then the skin thoroughly washed, neutralized and finished up as usual.

*Example 5*

A colloidal suspension is prepared as follows:

108 lbs. naphthalene
108 lbs. sulphuric acid 98%
are heated at 130° C. for 6 hours, then cooled to 90° C.

185 lbs. of a mixture of benzyl naphthalenes, obtained by the reaction of naphthalene and benzyl chloride in presence of zinc dust, are added, also
40 lbs. water
85 lbs. sulphuric acid 98%.

The temperature of the mixture is adjusted to 85° C. and held there while
90 lbs. formaldehyde 37%
are added very slowly with good stirring. The product is diluted somewhat, the excess of sulphuric acid neutralized with caustic soda solution, and the mixture finally diluted to 960 lbs.

100 lbs. chrome-tanned calfskins in the blue are placed in a drum with 250 lbs. water at 90° F. and 12% of the product prepared thus added. The drum is rotated for 1 hour, then the skins are washed, neutralized, and finished up as usual. In this way a strong well-filled piece of leather resistant to hot water, is obtained.

Having set forth and illustrated the nature of this invention I claim:

1. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing equimolecular proportions of naphthalene sulphonic acid and dibenzyl-naphthalene by means of formaldehyde in presence of sulphuric acid of non-sulphonating strength.

2. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing equimolecular proportions of naphthalene sulphonic acid and dibenzyl-naphthalene by means of formaldehyde in presence of a condensing agent.

3. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing equimolecular proportions of naphthalene sulphonic acid and dibenzyl-naphthalene by means of formaldehyde.

4. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing naphthalene sulphonic acid with dibenzyl-naphthalene by means of formaldehyde.

5. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing naphthalene sulphonic acid with a mixture of benzyl naphthalenes by means of formaldehyde.

6. The process of tanning with comprises treating skins with a colloidal suspension of a resinous product prepared by condensing a sulphonic acid derived from the class consisting of naphthalene and hydrogenated naphthalenes with a mixture of benzyl naphthalenes, by means of formaldehyde.

7. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing a sulphonic acid derived from the class consisting of naphthalene and hydrogenated naphthalenes, with a water-insoluble aromatic hydrocarbon from the class consisting of naphthalene and its derivatives, by means of formaldehyde.

8. The process of tanning which comprises treating skins with a colloidal suspension of a resinous product prepared by condensing a sulphonic acid derived from the class consisting of naphthalene and its derivatives, and a water insoluble aromatic hydrocarbon from the class consisting of naphthalene and its derivatives, by means of formaldehyde.

9. The process of tanning which comprises treating chrome-tanned skins with a colloidal aqueous suspension of a resinous product.

10. The process of tanning which comprises treating hides or skins with a colloidal aqueous suspension of a resinous product.

11. A process of tanning which comprises treating skins with a mixture of natural tannins and the product derived as set forth in claim 7.

12. The process of tanning which comprises treating skins which have already been tanned with the product derived as set forth in claim 7.

In testimony whereof I affix my signature.

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