

## UNITED STATES PATENT OFFICE

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## PROCESS OF TANNING

No Drawing.

Application filed May 25, 1931. Serial No. 540,009.

This invention relates to a process of tanning.

More specifically this invention relates to a process of tanning which includes treating the hides with a sulfonic acid body of the abietene family.

It is an object of this invention to improve the usual tanning processes, whereby to both accelerate the tanning action and improve the properties of the resulting leather, particularly as to color and texture.

Other and further important objects of this invention will become apparent from the following description and appended claims.

In the copending application of Gubelmann, Weiland, and Henke, Serial No. 431,629, filed on February 26, 1930, it is mentioned that when sulfonated abietene, abietine, abietane or other pyrogenic decomposition products of rosin, abietic acid or abietyl chloride, are added to aqueous treating baths for materials of the textile and leather industry, the efficiency of such baths is considerably increased. In other words, these sulfonic acids increase the wetting and penetrating powers of aqueous treating baths for both textile material and leather.

We have now found that when sulfonic acids of the above class are used in the tanning of hides, they not only increase the wetting power of the tanning bath, but also, in addition, act as tanning agents themselves and add to the action of the natural tanning agents or vegetable extracts normally used in such baths. In view of our discovery of this additive tanning action, the quantity of vegetable tanning agent required to produce a given effect upon a given weight of hide may be considerably reduced, being replaced by an equivalent quantity of the sulfonic acid compounds above mentioned. The tannin equivalent of abietene-sulfonic acid, as determined by the official method of the American Leather Chemists Association, was found to be from 40 to 50% per unit weight.

Moreover, the tanning power of the mixture, namely the vegetable tanning agent and sulfonic acid of the abietene family, considerably exceeds the powers of the indi-

vidual components, even if the latter be taken in quantity corresponding in tannin content to that of the entire mixture. Thus, in certain instances where the vegetable tanning agent alone requires 15 hours for completion of the tanning action, a mixture of the same vegetable extract with abietene-sulfonic-acid sodium salt, containing the latter in sufficient quantity to supply from 1.5 to 50% of the total tannin content, will complete the tanning action in about 2 to 4 hours, with superior effects as far as the texture and color of the resulting leather is concerned.

In this respect the action of our novel tanning agents or tanning assistants is somewhat analogous to the action of certain other synthetic tanning agents now on the market and known as "Syntans". Whereas, however, most of the "Syntans" possess high acidity which acts injuriously upon the leather and which therefore, prohibits their use in large concentration where their beneficial effects upon the tanning reaction might become pronounced to a useful degree, our novel tanning agents are characterized by low acidity and, moreover, they are active in the form of their neutral salts. Our novel agents may therefore be used in as high proportions as to replace 20 to 50% of the natural tanning agent. Since up to certain limits the beneficial effects upon the time of the tanning reaction and upon the texture and color of the resulting leather seems to increase as the ratio of abietene-sulfonic acid compound to the weight of the leather is increased, the above mentioned adaptability of our novel agents to be used in comparatively large concentrations is of greatest technical importance.

A further advantage of our novel tanning assistants over those now known in the art is that in many cases where the latter are not applicable at all or applicable only without any beneficial effects, for instance in the case of tanning sheepskin with chestnut, our novel assistants may be applied to great advantage, as will be readily seen from the specific examples below.

Our novel tanning agents may be defined generically as being sulfonation products of



pyrogenic decomposition products of rosin acids such as for example abietic acid, or their halides for instance abietyl chloride.

Due to variations in the source of the abietic acid containing material (rosin), the resulting product produced therefrom will vary slightly in its composition, but we believe that, independent of the source of the abietic acid containing material, the product obtained will contain a large proportion of a specific hydrocarbon, abietene or abietine. A number of these various products are described by Ruzicka, Helvetica Chimica Acta, volume 6, pages 838 to 840. We have tried sulfonated derivatives of many of these products and find that they are all useful for our purpose. However, exceptionally outstanding in this respect is the sulfonation product of a rosin-decomposition product obtainable according to the U.S. patent granted to Clyde O. Henke, No. 1,853,353, dated April 12, 1932. This procedure, briefly, consists of refluxing rosin in the presence of iron and at a temperature of about 350 to 375° C. until its acidity has been practically destroyed, and then distilling to recover a fraction boiling below 450° C. The hydrocarbon product thus obtained is characterized by a specific gravity of about 0.99 (at 20° C.) and its sulfonation product is characterized by exceptionally high wetting powers, and by yielding a sodium salt which is non-hygroscopic.

The methods of preparing these sulfonic acids are more specifically described and claimed in U. S. Patent No. 1,853,352 granted to Henke and Weiland, on April 12, 1932, and in the U. S. Patent No. 1,853,353 above referred to. Briefly, these methods consist of treating the above defined hydrocarbons of the abietene family with strong sulfonating agents, such as, sulfuric acid monohydrate, at temperatures between about 0 to 50° C.

We have also found that the sulfonation products of abietane which are more specifically described and claimed in U. S. Patent No. 1,853,348 granted to Gubelmann and Henke, on April 12, 1932, can be used in the same way as the sulfonation products of abietene. We believe the general ring structure of abietene and abietane to be the same, the specific difference being, that part of the unsaturation linkages of abietene are absent in abietane.

The sulfonic acids of the above products may be transformed into water soluble salts such as potassium, sodium and ammonium and in any of these forms, as well as in the form of free acid, may be used as assistants in tanning, with the improved effects above noted. For best results the said water-soluble salts should preferably be purified by extraction with benzol according to the copending application of Henke Serial No. 540,008 filed of even date herewith. This process consists, briefly, of agitating an aque-

ous solution of said water soluble salts with benzol, allowing the mass to settle into layers, and separating the organic layer from the aqueous layer, which contains the purified abietene-sulfonic acid body.

The following examples will serve more particularly to illustrate our invention. Parts given are parts by weight.

#### Example 1

To 1500 parts of water contained in a mill or drum are added 560 parts of sumac extract (containing 25% of tannin as determined by the official method of the American Leather Chemists Association for tannin analysis) and 20 parts of a 20% solution of abietene sodium sulfonate. The abietene sodium sulfonate for this purpose may be prepared from wood rosin of grade B or FF according to U. S. Patent No. 1,853,353 and the copending application of C. O. Henke, Serial No. 540,007, filed of even date herewith, and should be purified by extraction with benzol according to the copending application Serial No. 540,008 also filed of even date herewith. 1000 parts of pickled sheepskin are now introduced, and the mass agitated, as by revolving the drum, for a period of about 2½ to 4 hours. At the end of this period, the sheepskin will be found converted into tanned leather, superior in color and feel to leather obtained by the use of sumac extract alone. The product is also silkier in grain and fuller than leather prepared by the use of sumac alone.

If in the above example the abietene sodium sulfonate is omitted, the time required for tanning will be 12 to 15 hours and the product will not have the superior properties mentioned above.

The abietene sodium sulfonate not only shortens the time required for tanning and improves the leather but it may also replace a large amount of the natural tannin, as is illustrated by the proportions used in Example 2.

#### Example 2

To 1500 parts of water contained in a mill or drum are added 448 parts of sumac extract (25% tannin) and 112 parts of a 20 to 25% solution of abietene sodium sulfonate. After introducing 1000 parts of pickled sheepskin the drum is rotated for 2½ to 4 hours. At the end of this period the sheepskin will be found to be converted into tanned leather of a similar quality to that secured in Example 1.

It will be noted that in this example the total tannin content is less than in Example 1. Thus the addition of 112 parts of abietene sodium sulfonate solution enables one to eliminate an equal weight of sumac extract, although the abietene sodium sulfonate introduced contains only 40% of the tannin



content of the sumac replaced. In other words, the added abietene sulfonic acid compound, in addition to contributing tannin to the bath seems to increase the efficiency of the sumac extract.

#### Example 3

The procedure is the same as in Example 2 except that 390 parts of sumac extract and 364 parts of a 20 to 25% solution of abietene sodium sulfonate are used instead of the respective quantities specified as in Example 2. The results are substantially the same.

It will be noted that in this example the abietene sodium sulfonate contributes about 27% of the total tannin content of the tanning bath.

The sodium abietene sulfonate is also valuable for tanning skins other than sheepskins as is illustrated in Example 4.

#### Example 4

The tanning bath is prepared as in Example 1. 1000 parts of bated calf-skins are now introduced and the drum rotated as before. The resulting leather is of superior qualities as to color, feel, grain, and fullness.

The sodium abietene sulfonate can be used in conjunction with other vegetable tannins besides sumac as is illustrated in Example 5.

#### Example 5

To 1500 parts of water contained in a mill or drum are added 560 parts of chestnut extract containing 25% tannin and 100 parts of a 20% abietene-sodium-sulfonate solution. There is now introduced 1000 parts of pickled sheepskin and the drum is rotated for 2 to 4 hours. At the end of this period the skin has become converted into leather of superior qualities as to color, feel and grain.

It is remarkable that if chestnut extract be used as tanning material without the aid of our novel assistants, the skin cannot be added directly into the tanning bath but must be steeped in the water first, and the chestnut extract must be fed into this mass very gradually, so that the whole operation consumes about 15 hours. Violation of this precaution causes the skin to shrivel up and converts it into a practically useless product. This bad effect cannot be overcome by the addition of other tanning assistants or synthetic tanning materials now on the market to the tanning bath.

Instead of a salt of abietene-sulfonic acid in the above examples, the free acid may be used. Also, the free acids or salts of the sulfonic acids of abietine or abietane may be employed with equal success. The preparation of these compounds is described in the copending application of Gubelmann and Henke, Serial No. 431,626, filed February 26, 1930 and in the U. S. Patents Nos. 1,853,348 and 1,853,352. The derivatives obtained by

condensing the said sulfonic acids with formaldehyde may also be used with great success. These aldehyde condensation products are described and claimed in the copending application of Henke and Charlton Serial No. 540,010, filed of even date herewith.

The proportion of abietene-sulfonic acid body in the tanning bath may vary within wide limits. Satisfactory results may be obtained by using the abietene-sulfonic acid body in proportions up to about 50% of the total tanning material, expressed in terms of "tannin content". By the latter expression we mean that the equivalent tannin content contributed by the abietene-sulfonic acid body does not exceed 50% of the total equivalent tannin content of the mixture.

The proportion of abietene-sulfonic acid body may also be specified by reference to the weight of hide to be tanned. We found that a proportion of from 0.4 to 20% by weight of abietene-sulfonic acid body as compared to the weight of the moist hide to be treated gives satisfactory results.

Other and further modifications may be introduced into our invention without departing from the spirit of the same.

In the claims below it should be understood that by the term "sulfonic acid body of the abietene family" we mean to cover and include the product obtained by sulfonating any compound containing in its structure the abietene nucleus, as more particularly illustrated by abietene, abietine, abietane. Derivatives of these sulfonic acid bodies such as the formaldehyde or benzaldehyde condensation products thereof, or salts of such sulfonation products may also be used. By the term "hide" we mean to cover and include hides, skins, pelts, or any other form of animal skin.

We claim:

1. The process of tanning which comprises subjecting hide to the action of a bath containing a vegetable tanning agent and a member of the group consisting of sulfonic acid bodies of the abietene family, their salts and aldehyde condensation products.

2. The process of tanning which comprises subjecting hide to the action of an aqueous solution of a vegetable tanning agent and a member of the group consisting of sulfonic acid bodies of the abietene family, their salts and aldehyde condensation products.

3. The process of tanning which comprises subjecting hide to the action of an aqueous bath containing a mixture of vegetable tanning agents and a member of the group consisting of sulfonic acid bodies of the abietene family, their salts and aldehyde condensation products, the member of said group being present in a proportion not exceeding 50% of the total equivalent tannin content of the mixture.

4. The process of tanning which comprises



subjecting hide to the action of an aqueous bath containing a vegetable tanning agent and a member of the group consisting of sulfonic acid bodies of the abietene family, their salts and aldehyde condensation products the member of said group being present in a proportion not exceeding 20% by weight as compared to the weight of the hide.

5. The process of tanning which comprises subjecting hide to the action of an aqueous bath containing a vegetable tanning agent and a water soluble salt of abietene-sulfonic acid.

6. The process of tanning which comprises subjecting hide to the action of an aqueous bath containing a mixture of a vegetable tanning agent and a water soluble salt of abietene-sulfonic acid, the said salt of abietene-sulfonic acid being present in proportion not exceeding 50% of the total equivalent tannin content of the mixture.

7. The process of tanning which comprises subjecting hide in an aqueous bath containing a vegetable tanning agent and an alkali salt of abietene-sulfonic acid in a proportion not exceeding 20% by weight as compared to the weight of the hide.

8. As a new composition of matter, a tanning preparation comprising water, a vegetable tanning extract, and a member of the group consisting of sulfonic acid bodies of the abietene family, their salts and aldehyde condensation products.

9. As a new composition of matter, a tanning preparation comprising water, a vegetable tanning extract, and a water soluble salt of a sulfonic acid of the abietene family.

10. As a new composition of matter, a tanning composition comprising a vegetable tanning extract and abietene sulfonic acid.

11. As a new composition of matter, a tanning composition comprising sumac extract and abietene sodium sulfonate.

In testimony whereof, we have hereunto subscribed our names at Milwaukee, Milwaukee County, Wisconsin.

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AUGUST C. ORTHMANN.

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