

## UNITED STATES PATENT OFFICE

2,653,967

TANNING MATERIALS AND PROCESS FOR  
PREPARING THE SAMEKenneth Potter Monroe, Boston, Mass., assignor  
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Mass., a corporation of MassachusettsNo Drawing. Application March 20, 1951.  
Serial No. 216,655

7 Claims. (Cl. 260—473.5)

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The present invention relates to tanning materials derived from natural sources and characterized by the production of relatively light colored tanned products such as leather.

The invention relates more particularly to "bleached" tanning materials which contain a polyphenolic group such for example as are derived from quebracho colorado, wattle, cutch, mangrove, and the like.

It has long been the practice to employ aqueous extracts of certain natural tanning materials of the above mentioned type and particularly those derived from the tree known as quebracho colorado for producing the so-called vegetable tanned "leathers."

Quebracho extract is manufactured in very large quantities in various parts of the world, but more particularly in South America, where the quebracho wood is chopped up and extracted with water, the extract then being evaporated under vacuum to produce what is known as quebracho extract. As this is somewhat deficient in solubility in water, it has long been the custom to treat it with upward of about 3% of its weight of sodium bisulfite or sodium sulfite to produce what is known as a water-soluble ("clarified") quebracho extract. This extract as it appears on the market is from a brown to a very dark brown in color and yields correspondingly dark colored solutions. Leather tanned with such solutions also has a characteristic reddish color which, however, has been generally accepted by the tanning industry as characteristic and hence more or less unavoidable.

Numerous attempts have been made to produce a quebracho extract yielding a lighter colored leather and recourse has been had to the treatment of such extracts with agents such as are exemplified by sodium formate and sodium hydrosulfite. However, the extracts thus produced, while yielding leathers somewhat lighter in color, have not yielded leathers by any means as light as are often desired.

It is therefore the object of the present invention to produce "bleached" extracts of the quebracho type which are characterized by producing much lighter colored tanned products, such as leather.

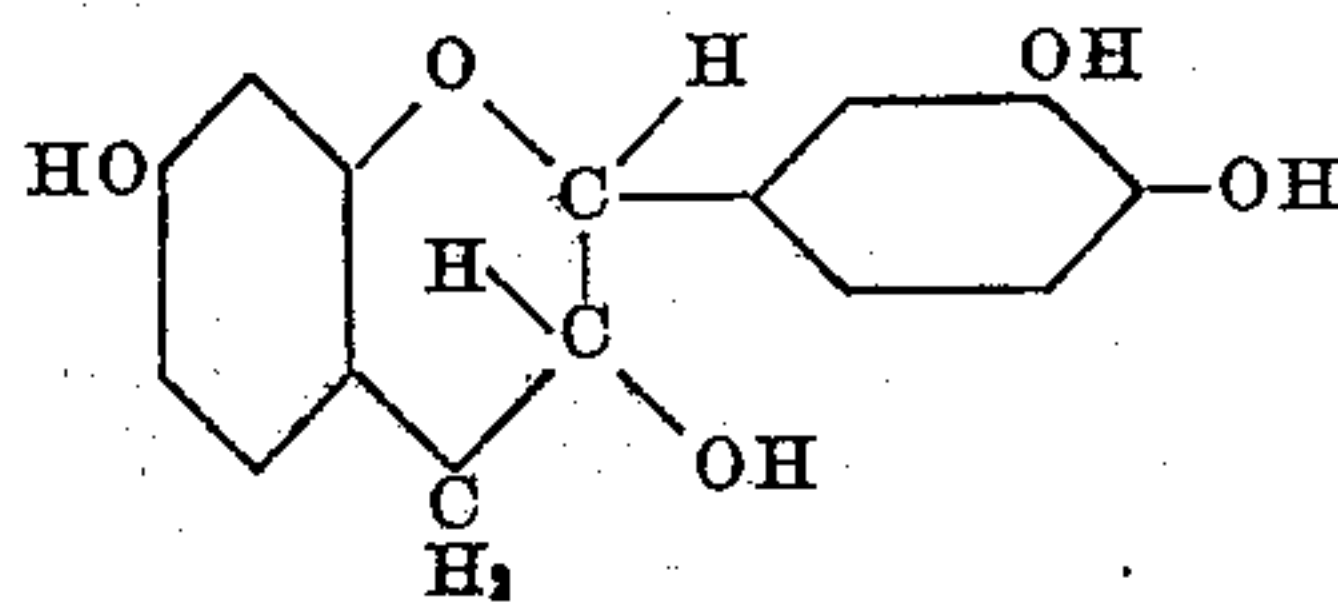
The tanning materials of the quebracho, wattle, clutch, and mangrove types have certain properties in common, namely, that they contain complicated compounds which are of a polyphenolic nature, it having been determined with a considerable degree of certainty that each typical molecular unit of these compounds contains

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at least one catechol group which is in essence orthodihydroxybenzene. Now, it is known that compounds of this general type are readily oxidizable so as to produce quinone types of products which are much darker in color than are the dihydroxy compounds. The object of "reducing or bleaching" this natural tanning extract was to reduce the substituent oxygen atom of the quinone back to the hydroxyl or OH group so as to reconstitute as far as possible the polyphenolic radicals in about the form in which they occurred in the tree before it was chopped down and the tanning material extracted therefrom.

It has now been discovered, however, that by carrying out the "bleaching" in the presence of small, practically catalytic, amounts of a vanadium compound, that an end product is obtained which will produce much lighter colored tanned products, such as leather, than will similar compounds which have not been "bleached" in the presence of these small amounts of vanadium compounds.

For the purposes of the present invention the types of vanadium compounds in which the vanadium plays the role of an acid-former, that is a role analagous to a nonmetal, appear to give excellent results. Particularly useful are the alkali meta-vanadates. By the term "alkali" in the present connection it is to be understood that this is to include the alkali metals themselves as well as ammonium. The extract of quebracho colorado contains as its major constituent a compound which contains two benzene rings, one of which apparently has one phenolic hydroxyl group and the other one has two phenolic hydroxyl groups in the ortho position relative to each other. It is generally believed that the configuration of the fundamental and essential tanning constituent in quebracho extract has the structural formula:



In the further description hereinbelow I have adopted the letter T as an abbreviation of the above mentioned complex structural formula, (the polycyclic atomic skeleton of which contains at least two benzene or symmetrical six-membered carbon atom rings and also one heterocyclic ring usually containing oxygen) and have indicated in parentheses and by the sub n

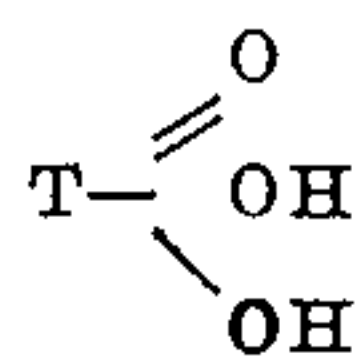


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the number of phenolic hydroxyl groups attached to one molecular unit. The aliphatic hydroxyl group attached to the aliphatic heterocyclic ring is neglected since it possesses a wholly different chemical reactivity which renders it inert under the practice of this invention.

In these compounds designated as  $T(OH)_n$ ,  $n$  has a value of at least two, but may be three or more. As will be seen from the above molecular configuration given for quebracho, the phenolic hydroxyl groups need not be and usually are not linked to the same benzene ring.

Considering therefore that the material as originally extracted and while comparatively fresh would consist of  $T(OH)_3$ , this probably becomes oxidized by the effect of atmospheric oxygen and light to  $T(OH)_2O$  or as better exemplified by the following structural formula:



This oxidation occurs during the interval, which may be from months to years, between the cutting down of the trees and the actual extraction of the tanning materials therefrom. The oxidation invariably continues during the unavoidable exposure to air and light during the extraction and shipping of the extract. Producers of the natural polyphenolic tanning material such as quebracho, wattle, cutch, and mangrove, have always experienced this hitherto unavoidable difficulty.

It is possible, however, to reduce the substituent oxygen atom in these compounds back to a hydroxyl group by the use of a sufficiently powerful reducing agent. One of these is sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , although other equivalent reducing agents may, of course, be used.

In accordance with the present invention I therefore treat quebracho extracts (and I am using this in its generic sense) with such a reducing agent and/or other agents plus, however, small amounts of a vanadium compound which appears either to (a) accelerate the reduction or (b) enable a more drastic reduction to a different end product which has superior resistance to deterioration by air and light, or (c) form a chromophoric blue "chelate" complex with the components of the "bleached" tannin, so tending to lighten the color of the leather somewhat as ordinary household "bluing" tends toward a whiter wash.

I do not wish to be bound by any particular theory but state as the empirical fact that the vanadium compounds, particularly in the initial form of a canadate, will accomplish the desired results.

This "bleaching" in the presence of the vanadium compound may be accomplished in a number of different ways of which I shall give two examples, as follows:

## Example 1

3000 grams of a so-called "regular" quebracho extract containing about 40% of solids and manufactured by treating the so-called "solid" raw quebracho extract which contains about 20% of water with 3% of its weight of sodium bisulfite by the conventional method in order to "solubilize" the quebracho, was weighed into a four liter beaker equipped with an efficient stainless steel agitator and a thermometer. The beaker was suitably heated, for example in a water bath, the stirrer was started, and 45 grams of sodium

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formate were added to the extract, which at that time was at a temperature of about 45° to 50° C. The sodium formate readily dissolved under the influence of the agitation. There was then added one-tenth of one gram of ammonium meta-vanadate previously dissolved in 10 milliliters of water, whereafter the temperature of the resulting mixture was raised to a temperature within the range of from about 90° to 95° C., this requiring about thirty minutes, whereafter the agitation was continued within the said range for one hour more. Thereafter the material was cooled down to room temperature. The extract had lost its original reddish color, and pieces of skin tanned therewith were effectively tanned to produce much lighter colored leather than would be obtainable from quebracho extracts which had been reacted without the presence of the vanadium compound.

## Example 2

3000 grams of the "regular" quebracho extract, as above mentioned, were weighed into a four liter beaker, equipped with an efficient stainless steel agitator and thermometer, and heated in a water bath. Agitation was started at a moderate speed and when the temperature had attained 45° to 50° C. there were added in the order mentioned:

1. 60 grams of sodium formate
2. 16 grams of sodium hydroxide, previously dissolved in 25 milliliters of water
3. 45 grams of sodium hydrosulfite
4.  $\frac{1}{4}$  of 1 gram of ammonium meta-vanadate previously dissolved in 25 milliliters of water

The temperature was then raised to 90° C. within thirty minutes and maintained between 90° and 95° C., with continued vigorous agitation for about one hour, whereafter the thus reduced extract was cooled to room temperature. In this manner also a quebracho extract was obtained which had lost its initial reddish color, and which yielded a light colored leather when a piece of skin was tanned therewith.

Generally speaking the amount of vanadium compound necessary is of a very low order and may be as little as 0.003% by weight, of the quebracho extract; in any event the amount is of an order which could readily be considered as catalytic in amounts, although I do not wish to commit myself to any particular theory as to the reason for the production of the results. In the hereunto appended claims the statement of small amounts is intended to mean amounts about on the order stated and generally within the range of from about 0.003% to about 0.5%. Larger amounts do not appear to produce any further enhancement of the results.

While ammonium vanadate has been used in the particular example, it may be stated that other corresponding water-soluble vanadium compounds may be employed, probably by reason of the fact that the strong reducing agents employed such as the sodium hydrosulfite will reduce the vanadium compounds to the vanadyl state so that in the presence of the sodium hydroxide, for instance in Example 2, the vanadyl compounds will be formed in the reacting mixture. Therefore I do not wish to be circumscribed and limited to the use or direct introduction of ammonium metavanadate. Undoubtedly in the presence of the other alkaline materials other vanadates such as sodium vanadate may be formed. By reason of the fact that such small quantities are employed, it is difficult definitely to



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determine the true condition of the vanadium in the ultimate composition. Whether it unites with some of the phenolic groups or other constituents of the tanning compositions is not at present known. In any event, the essential principle of the present invention involves the "bleaching" of natural tanning materials containing polyphenolic groups with reducing agents and/or with other reagents in the presence of a vanadium compound, and I therefore desire to have my claims construed with this in view.

I claim:

1. Process of producing a tanning composition which comprises subjecting quebracho extract to the conjoint action of sodium formate and ammonium meta-vanadate.

2. Process of producing a tanning composition which comprises subjecting quebracho extract to the conjoint action of sodium formate, sodium hydroxide, sodium hydrosulfite and ammonium meta-vanadate.

3. Process of producing a quebracho extract characterized by yielding relatively light colored tanned products which comprises heating solubilized quebracho extract in water with sodium formate and a small amount of an alkali vanadate.

4. Process of producing a quebracho extract characterized by yielding relatively light colored tanned products which comprises heating solubilized quebracho extract in water with sodium formate and a small amount of ammonium vanadate.

5. Process of producing a quebracho extract characterized by yielding relatively light colored

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tanned products which comprises heating solubilized quebracho extract in water with sodium formate, sodium hydroxide, sodium hydrosulfite and ammonium vanadate.

6. Process of lightening the color of natural occurring tanning materials from the group consisting of quebracho, wattle, clutch, and mangrove which comprises treating the same with a small, catalytic amount of an alkali vanadate, and a reducing agent from the group consisting of sulfites, hydrosulfites and formates.

7. A tanning material from the group consisting of quebracho, wattle, clutch and mangrove, the color of which has been lightened by treatment with small, catalytic amounts of an alkali vanadate, and a reducing agent from the group consisting of sulfites, hydrosulfites and formates.

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