

UNITED STATES PATENT OFFICE.

ALPHONSE SEYEWETZ AND LOUIS MEUNIER, OF LYON, FRANCE.

TANNING.

987,750.

Specification of Letters Patent.

Patented Mar. 28, 1911.

No Drawing.

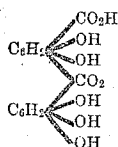
Application filed January 29, 1908. Serial No. 413,272.

To all whom it may concern:

Be it known that we, ALPHONSE SEYEWETZ and LOUIS MEUNIER, citizens of the French Republic, residing at Lyon, in France, have invented certain new and useful Improvements in Tanning, of which the following is a specification.

The present invention is based upon the following observations:—1. If a skin is tanned with gallo-tannic acid or tannin produced from the gall-nut, in the absence of alkali and oxygen, the product obtained has the appearance of leather, very slightly colored, but is gelatinized by the action of hot water; the product is, therefore, not a true leather. 2. If a skin is tanned with gallo-tannic acid under conditions favorable to the oxidation of the latter, the acid being agitated while in contact with air, preferably in the presence of alkali, a colored leather is obtained which resists the action of boiling water and has the properties of properly tanned leather.

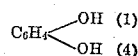
The molecule of gallo-tannic acid $C_{14}H_{10}O_9$ comprises in addition to carboxyl or acid-forming groups ($-\text{COOH}$), easily oxidizable phenolic groups ($-\text{OH}$)



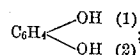
and since unoxidized phenols of this character do not tan while oxidized or oxidizing phenols do tan, it appears that the tanning action is more particularly due to the oxidation of these phenolic groups. We have also found that other phenolic compounds and in particular those derived from the benzenoid hydrocarbons used under conditions favorable to their oxidation are capable of converting skin into true leather. This result can be obtained, in a greater or less degree, with a large number of simple and complex phenols, and also with their substitutive derivatives.

Of the compounds which give the best

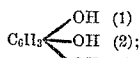
results the following may be cited:—hydro- 50
kinone



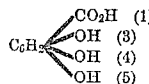
its homologues and products of substitution; 55
pyrocatechin



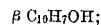
pyrogalllic acid



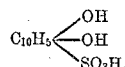
gallic acid



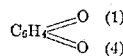
β naphthol



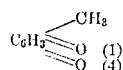
sulfonic dioxynaphthalin



Proceeding from these observations, and more particularly from that which indicates that the phenols must be oxidized in order to combine with the dermal substance, we also investigated the question as to whether the products of direct oxidation of these phenols, that is products formed by an oxidation insufficient to destroy the cyclic structure of the phenol, more particularly the kinones and their derivatives, are capable of directly combining with dermal fiber to convert the same into leather without the co-action of free oxygen. With regard to these products of oxidation of the benzenoid hydrocarbons it has been found that ordinary kinone



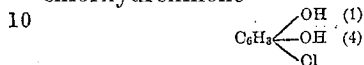
and its homologues, such as tolukinone



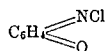
both of which may be regarded as oxidation products of phenols, yield very remarkable results and are capable, even when used

in very small quantities, of forming with skin imputrescible compounds which perfectly resist the action of boiling water, have great strength and suppleness, and constitute in fact true leather.

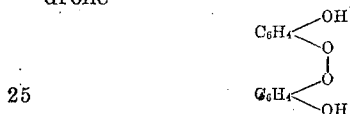
The kinones derived from the products of substitution of hydrokinone, for example the derivative obtained by the oxidation of chlorhydrokinone



(the adurol of commerce), behave in the same way as ordinary kinone. Kinone chlorimid



also has the same tanning properties as kinone. The intermediate oxids, between the kinones and phenols, such as quinhydrone



are also capable of converting dermal matter into leather.

The tanning action is specifically different with the various phenolic materials employed. Where these bodies oxidize rapidly, as in the case of hydrokinone, the action is rapid; where they oxidize with greater difficulty, as in the case of resorcin, the action is slower. The tanning action being dependent upon the presence of the oxidized bodies, obviously it is quicker where the aqueous tanning solution is made of preformed oxidation products than when oxidation and tanning go on simultaneously; and particularly with difficultly oxidizable phenols. The tanning power of these oxidation products is remarkable. The kinones and kinhydrones or quinhydrones, derived from the direct oxidation of phenols carrying two OH groups in the ortho or para position, and particularly the latter, when dissolved in water rapidly transform hide into imputrescible leather resisting the action of boiling water. One part of ordinary kinone or quinone, for example, suffices to tan 100 parts of hide, producing an insolubility which can only be realized by at least 35 to 40 parts of any of the ordinary tannins.

The present method of tanning can of course be employed in conjunction with ordinary tanning methods.

Examples will now be given, firstly of the use of kinones and their substitution products and kinone chlorimid, and secondly of the use of phenols.

Example I. Direct tanning with kinones, substitution products and kinone chlorimid.—As an example may be taken ordinary kinone applied to the tanning of calf-skin. For 100 kilos of soft, untanned skin, approximately 400 grams of kinone are dissolved in 100 liters of water and gradually added, at intervals, to the skin placed in a vat having an agitator, or preferably in a rocking or turning drum. It will be found that the tanning proceeds with remarkable regularity and with a drum turning say 10 revolutions per minute the tanning may be completed in 5 hours. With sheep-skins, incisions show the tanning to be complete throughout. The skin first acquires a pink tint, and then successively violet and brown colors. At the same time it swells appreciably. Agitation assists the propagation of the tanning action in the interior of the skin. The length of time required is considerably shorter in the case of kinone than in the case of hydrokinone in alkaline liquor and in contact with air (Example II). Approximately three days are required if the agitation only takes place at intervals, but the period may be modified by modifying the concentration of the kinone liquor. After the tanning the skin is dyed, dressed and finished as in the case of chrome leather, according to the particular purpose for which it is required. Sheep-skins may be treated in the same manner. Taking 100 kilograms of sheep-skin freed of wool, rinsed and dried, the material may be introduced into a rotating drum provided with a hollow shaft and the kinone solution introduced through this shaft in such quantity as to represent about 400 grams of kinone. This amount of material may be dissolved in 100 liters of water. The first additions are to be made gradually and in small portions while the latter may be added more rapidly. While kinone is soluble in water only to the extent of about half a per cent., this solubility is amply sufficient for the present purposes.

Example II. Tanning with phenol derivatives.—As an example may be taken hydrokinone applied to the tanning of sheep's skin in the presence of alkali and in contact with air. For 100 kilograms of skin 350 grams of hydrokinone are dissolved in water with 500 grams of crystallized carbonate of soda. The skin is placed in a vat having an agitating device to aid in aeration and oxidation, and is covered with water. The alkaline solution of hydrokinone is gradually added, with energetic stirring, and is allowed to act until the skin has acquired a violet brown color. The normal period required is approximately 24 hours,

but this may be reduced by increasing the agitation and thus assisting oxidation. The skin is then washed with water to remove the alkali. This method of tanning can also be successfully used with chromic acid as the oxidizing agent. In this case a chrome salt is formed, and assists the tanning action of the hydrokinone. The dyeing, dressing and finishing operations are performed in the same manner as in the case of chrome leather. It must, however, be mentioned that for dyeing the leather tanned by the methods described it is not necessary to previously mordant the same with sumach, as in the case of chrome leather, since the skin has great affinity for the coloring matter. Skins already tanned with chrome can even be successfully mordanted by means of kinone or its derivatives, with results comparable to those obtained with sumach. In tanning with preformed oxidation products of phenols, such as kinhydrone or quinhydrone, the operation is conducted exactly as previously described in the case of ordinary kinone, except that the kinhydrone may be used in the form of a powder in a bag attached to the manhole or other convenient portion of the interior of the rotating drum, kinhydrone being only slightly soluble in water. And, as in the case of kinone, the proportions of kinhydrone required will vary according to the use to be made of the leather. About 300 to 800 grams are used, this depending upon the leather to be made. It may be noted in this connection that kinhydrone when dissolved in water behaves for the present purposes as if it were a mixture of the solutions of kinone and hydrokinone.

The oxidation products of the substitutive phenols, such as the sulfonated derivatives, may be employed. Salts of these derivatives may also be used. For instance, benzokinone sulfonic acid is useful and may be employed as a sodium salt. It is very soluble in water, possesses no odor and does not exercise any irritating action. It has to be used in somewhat greater proportions than ordinary kinone, as, for instance, from 600 to 1,000 grams per 100 kilograms of hide. Using this substance the skin takes a red color different from the violet color given at one state of the tanning with ordinary kinone. This substance is to be added very slowly as it is rapidly fixed by the hide. The addition with sheep-skin may last over a period of 7 to 8 hours. It should not be employed in a bag in a solid state. Sulfonated hydrokinone may be used in an advantageous way, by dissolving in an alkaline solution and permitting free contact with air. About 500 grams of the sulfonated hydrokinone

suffice for 100 kilograms of hide. The details of operation are as before. The hide tans very well but the color after tanning is somewhat redder and less violet than is the case in using the non-sulfonated hydrokinone.

Using these new tanning agents it is found that in general vat tanning is better for leathers requiring a certain degree of suppleness, such as strap and harness leather, etc. Suspension tanning is better for leathers requiring a certain firmness, such as sole leather.

The exact proportion of the new agents to be used will depend upon the use to be made of the leather. The greater the resistance which it is to offer to water the greater the amount of the tanning agent which must be employed. If a subsequent tanning with another substance is to be used, the proportions are of course reduced somewhat. In the case of sole and strap leathers double tanning is often advantageous, for instance tanning first with kinone and then with tannin, since it permits diminishing very considerably the length of time required for tanning as compared with the time required where only vegetable tanning materials are employed. The leather so produced is also heavier since the kinone has the property of permitting a remarkable increase in the amount of the vegetable extract absorbed in the later operation. The increase in amount of leather produced may be from five to ten per cent. Leathers with these mixed tannings resist the action of water very well.

Leather prepared by the process set forth has the following characteristics.

1. Great thoroughness of tanning, giving it great power of resisting the action of water, even boiling water, notwithstanding the small proportion of tanning matter used.
2. Great softness to the touch, sheep's leather being rendered almost as soft as chamois leather.
3. Great durability.
4. Great affinity for coloring matter, which obviates the use of sumach, injurious to the grain of the leather.

What we claim as our invention and desire to secure by Letters Patent of the United States is:—

1. The process of tanning which comprises treating hide with oxidation products of a phenol, said products having a cyclic structure.

2. The process of tanning which comprises treating hide with oxidation products of a phenol, said products having a cyclic structure, while simultaneously producing said oxidation products.

3. The process of tanning which comprises treating hide with oxidation products

of a phenol, said products comprising a kinone.

4. The process of tanning which comprises treating hide with oxidation products
5 of a phenol, said products comprising a substance of the kinone type and having a cyclic structure.

In witness whereof we have signed this specification in the presence of two witnesses.

ALPHONSE SEYEWETZ.
LOUIS MEUNIER.

Witnesses:

GASTON JEANNIAUX,
THOS. N. BROWNE.