

UNITED STATES PATENT OFFICE.

ADOLF RÖMER, OF STUTTGART, AND LOUIS BLANGEY, OF MANNHEIM, GERMANY,
ASSIGNORS, BY MESNE ASSIGNMENTS, TO THE CHEMICAL FOUNDATION, INC., A
CORPORATION OF DELAWARE.

TANNING.

1,421,722.

Specification of Letters Patent.

Patented July 4, 1922.

No Drawing. Original application filed September 2, 1916, Serial No. 118,286. Divided and this application filed April 27, 1917. Serial No. 165,000.

To all whom it may concern:

Be it known that we, ADOLF RÖMER and LOUIS BLANGEY, citizens of the German Empire and of the Swiss Republic, respectively, residing at Stuttgart and Mannheim, Germany, have invented new and useful Improvements in Tanning, of which the following is a specification.

The present invention relates to certain improvements in tanning with artificially produced tanning materials and is divided out from our co-pending application Serial Number 118,286, filed September 2, 1916, for the same invention.

As is known, the vegetable tanning materials employed for tanning hides without exception possess an amorphous character. In our original application Serial No. 118,286, filed September 2, 1916, we have described that we can transform hides into a valuable leather by means of organic bodies which contain sulfonic or carboxylic acid groups or both these groups, having a crystalline character and being soluble in water and capable of precipitating glue or gelatine from solutions thereof. The object of the present invention is to make specific claims for tanning with a group of compounds of the aforesaid character which is characterized by being prepared without the action of formaldehyde and therefore containing no CH_2 -groups connecting two or more aromatic nuclei.

The bodies can be used for tanning either alone or together with natural or synthetic tanning materials of other kind or mixed with non-tanning materials.

The process of tanning can be carried out in watery solution in the usual manner and in order to further illustrate the invention by distinct examples we mention in the following a number of substances which can be used for the purpose of the present invention and, inasmuch as necessary, the process by which they can be prepared, but the invention is of course not confined to the use of the compounds quoted. The parts are by weight.

Example 1.

Dissolve 228 parts of 4,4'-dihydroxy-diphenyl-dimethyl-methane (see Annalen der Chemie, vol. 343, p. 85) in 1200 parts of dry nitrobenzene and add, whilst stir-

ring, 234 parts of chloro-sulfonic acid, at a temperature of $0-5^\circ \text{C}$. Allow to stand for several hours, blow out the hydrogen chlorid dissolved by a current of air, then pour the mass into water, separate the nitrobenzene and neutralize the aqueous solution with barium carbonate. The solution of the barium salt is filtered off and evaporated until crystallization begins. The barium salt which separates out is washed with a little cold water and transformed into the free sulfonic acid by treating with exactly the required quantity of diluted sulfuric acid. The liquid is then filtered and evaporated in vacuo at about 80°C .; the free sulfonic acid is hereby obtained in the form of a syrupy mass which solidifies to a crystalline mass when having been allowed to stand for some time. The watery solution of this acid can be used for tanning in the usual manner.

In quite an analogous manner a sulfonic acid of 4,4'-dihydroxy-3,3'-dimethyl-diphenyl-dimethyl-methane (Annalen der Chemie, vol. 400, p. 33) can be obtained.

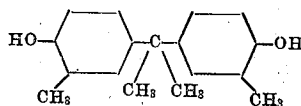
Example 2.

A tanning bath is prepared by dissolving in water—together, if desired, with suitable other components—a sulfonic acid as can be prepared by treating the condensation product of meta-cresol, para-cresol or alpha-naphthol and acetone (Annalen der Chemie, vol. 388, p. 304; Berichte der Deutschen Chemischen Gesellschaft, vol. 25, Referate p. 336) with fuming sulfuric acid or chloro-sulfonic acid.

Example 3.

Hides can be tanned by using a sulfonic acid prepared as follows.

128 parts of 4,4'-dihydroxy-3,3'-dimethyl-diphenyl-dimethyl-methane possessing the formula



are treated for several hours on the water-bath with 252 parts of crystallized sodium sulfite dissolved in 1000 parts of water and 100 parts of 30% formaldehyde until a test when acidified gives no longer a precipi-

tate. The solution is then acidified by adding hydrochloric acid whereupon 125 parts of crystallized barium chlorid are dissolved therein. When cold, the barium salt which has separated out, is filtered off, re-crystallized if necessary and converted, in the usual way, into the free sulfonic acid or its sodium salt, the latter representing an easily crystallizing compound. The free sulfonic acid can serve for tanning directly, the sodium salt after being acidified. With the watery solution of this substance, the tanning process can otherwise be effected in the usual manner.

Example 4.

Treat hides in the usual way with an aqueous solution of 5.5'-dihydroxy-2.2'-dinaphthylamine-7.7'-disulfonic acid (obtainable according to Example 2 of German Letters Patent No. 114,974).

Example 5.

50 parts of 4.4'-dihydroxy-benzophenone (Annalen der Chemie, vol. 218, p. 354) are dissolved in 200 parts of monohydratic sulfuric acid, then 150 parts of fuming sulfuric acid containing 23% SO₃ are added and the mixture is stirred at ordinary temperature, until a test is clearly soluble in water. The sulfonic acid can be obtained in a pure free state by decomposing its barium salt by the required quantity of sulfuric acid; the aqueous solution thereof can be used directly for tanning.

Example 6.

Treat hides in the usual way with an aqueous solution of anthraquinone-beta-sulfonic or 2.6-disulfonic acid or 1.4-dichloro-anthraquinone sulfonic acid, or hydroxy- or nitro-anthraquinone sulfonic acids or naphthantraquinone sulfonic acids or with the respective salts in the presence of acid.

While compounds such as the afore-described, possessing the above stated characteristic properties and containing in their molecule more than one aromatic nucleus connected by one or more polyvalent atoms, are particularly suitable for the claimed process, other compounds containing sulfonic or carboxylic acid groups and capable of precipitating glue, or gelatine, solutions are also suitable for the purpose of the present invention. Instances of such compounds are naphthol- or naphthylamine sulfonic acids capable of precipitating glue, such as 1.4-naphthol sulfonic acid, 2.6-naphthol-sulfonic acid, 1.2.4- or 2.1.5- naphthylamine-disulfonic acids, etc.

It is, of course, to be understood that the claims are intended to cover the solutions of the respective salts of the acids specified in the claims, preferably in acid solution, as well as such acids themselves.

The following procedure sets forth an illustrative embodiment of a manner in which my invention may be carried into practice:

100 parts of a sulphonic acid prepared as set forth in the above examples may be dissolved in about 1600 parts of water. Hides which have been limed and bated are introduced into a vat containing the tanning solution prepared as above and allowed to remain therein for a period of from 8 to 12 days. The leather thus obtained is subsequently dried and may be treated with fat in the usual manner.

We claim:

1. The process of tanning which comprises treating hides with a water-soluble aromatic compound of crystalline structure consisting of more than one aromatic nucleus connected to at least one carbon atom which is itself joined to at least one alkyl group and containing a mineral acid group, said compound being capable of precipitating glue from solutions thereof, substantially of the character described.

2. The process of tanning which comprises treating hides with a water-soluble aromatic compound of crystalline structure consisting of more than one aromatic nucleus connected to at least one carbon atom which is itself joined to at least one alkyl group and containing a sulphonic acid group, said compound being capable of precipitating glue from solutions thereof, substantially of the character described.

3. The process of tanning which comprises treating hides with a water-soluble aromatic compound of crystalline structure consisting of at least two aromatic nuclei connected to at least one carbon atom which is itself joined to at least one alkyl group and containing a mineral acid group, said compound being capable of precipitating glue from solutions thereof, substantially of the character described.

4. The process of tanning which comprises treating hides with a water-soluble aromatic compound of crystalline structure consisting of at least two aromatic nuclei connected to at least one carbon atom which is itself joined to at least one alkyl group and containing a sulphonic acid group, said compound being capable of precipitating glue from solutions thereof, substantially of the character described.

5. The process of tanning which comprises treating hides with a watery solution of a crystalline sulfonic acid derived from anthraquinone, substantially of the character described.

In testimony whereof we have hereunto set our hands.

ADOLF RÖMER.
LOUIS BLANGEY.