

UNITED STATES PATENT OFFICE.

WILHELM DIETERLE, OF FEUERBACH, GERMANY, ASSIGNOR TO J. HAUFF,
OF SAME PLACE.

PROCESS OF REMOVING LIME FROM AND SWELLING ALL KINDS OF SKINS OR HIDES.

SPECIFICATION forming part of Letters Patent No. 580,211, dated April 6, 1897.

Application filed December 13, 1894. Serial No. 531,695. (No specimens.) Patented in France September 20, 1894, No. 243,023; in Belgium November 17, 1894, No. 112,738; in England November 21, 1894, No. 22,546; in Austria December 18, 1894, No. 44/6,423; in Italy December 31, 1894, XXIX, 378,601, and LXXIV, 189, and in Hungary June 6, 1895, No. 2,939.

To all whom it may concern:

Be it known that I, WILHELM DIETERLE, a citizen of Württemberg, in the Empire of Germany, and a resident of Feuerbach, in Württemberg, Germany, have invented certain new and useful Improvements in Processes of Removing the Lime From and Swelling All Kinds of Skins or Hides, (for which Letters Patent were granted to me or by and with my consent to Julius Hauff in Great Britain, No. 22,546, dated November 21, 1894; in France, No. 243,023, dated September 20, 1894; in Belgium, No. 112,738, dated November 17, 1894; in Austria, No. 44/6,423, dated December 18, 1894; in Italy, XXIX, No. 378,601, and LXXIV, 189, dated December 31, 1894, and in Hungary, No. 2,939, dated June 6, 1895,) of which the following is a specification.

This invention relates to an improved process of treating hides and skins, so as to remove the lime from and produce the swelling of the same.

Free sulfuric acid does not form a suitable means for freeing skins and hides from lime on account of its caustic properties. I have found, however, that the sulfonic acids of the cresols, all of which form soluble lime salts, may be advantageously employed in tanning as a bate for freeing the skins and hides from lime, first, because in these acids the caustic properties of the free sulfuric acid are neutralized, and then again because they possess more or less antiseptic and albumen-coagulating properties, thus preserving the skins before and during the tanning.

A solution or mixture of the cresol sulfonic acid with water in the proportion of one to five hundred is advantageously employed. Into this solution the skins are placed at a temperature of about 30° centigrade and allowed to remain from one to two hours, according to the weight of the skins, the said solution or the skins being agitated by suitable means during this time. After this operation all lime will be found to have been extracted from the skins.

When freeing skins from lime which have not been previously scraped—that is, skins

possessing their full amount of lime—a mixture of the cresol sulfonic acid with varying quantities of free sulfuric acid can be advantageously employed—such as, for instance, the mixture which occurs as a crude product in the manufacture of the sulfonic acids. In this case the free sulfuric acid will act first on the lime on the surface or upper layer of the skin and neutralize the same immediately, so as to form gypsum, which latter may by subsequent treatment be rinsed off the skin. Not until this neutralization of the free sulfuric acid has taken place will the sulfonic acid be able to act on the lime in the lower layer of the skin so as to entirely dissolve the same. After the skin or hide has been freed from lime the swelling process may take place in a fresh solution of sulfonic acid and water in the proportions one to five hundred, which is necessary for the purpose of preparing sole-leather. As the sulfonic acids, on account of their marked properties of coagulating albumen, exert no dissolving effect on the substance of the skins or hides themselves, this treatment gives a very favorable result in respect of weight. Owing to the entire removal of the lime from the body of the skins, and owing to the sterilizing and hardening of the tissues which take place during the corroding operation, the leather obtained by the present process attains great strength and has a soft grain and a light color.

The following cresol sulfonic acids and the proportions used may serve as examples for the application of my process: (a) orthocresol sulfonic acid; (b) metacresol sulfonic acid; (c) paracresol sulfonic acid; (d) a mixture of the sulfonic acids of the isomer cresols.

The sulfonic acids of the isomer cresols are important representatives of the sulfonic acids which may be used for the antiseptic bating of hides and skins, owing to the facility of their production, the facility of obtaining the crude material, their cheap price, and essentially to their eminent antiseptic properties. These cresols are obtained in great quantities mixed with small quantities of phenol and xylenol as by-products in the

manufacture of carbolic acid. By treating them with concentrated or sulfuric acid and heating them to 100° centigrade they are readily changed into mono and di sulfonic acids, which have proven themselves excellent materials for neutralizing the lime in hides and skins.

The bate is obtained directly from crude cresol by mixing one hundred kilograms of cresol with from two hundred to three hundred kilograms of sulfuric acid of ninety-six per cent. and heating the mixture for several days in the water-bath, and then adding three hundred liters of water and allowing it to stand until the gummy impurities are separated and the pure solution obtained. Of this solution from two to three liters are dissolved in one thousand liters of water for every one hundred to one hundred and fifty kilograms of hides or skins and agitated with the latter for two hours at 130° centigrade, when the hides or skins are obtained entirely free from lime. The antiseptic property of cresol sulfonic acid is so considerable that the bating liquor can be permitted to stand for several weeks without the least deterioration or decomposition. For this reason the same liquor can be used by addition of new quantities of cresol sulfonic acid for a number of operations. The bating liquor has only then to be replaced by an entirely new liquor when mechanical impurities in considerable quantities are collected in the same.

With the same result the waste products of the manufacture of carbolic acids can be used, as these consist, mainly, of cresols, and the so-called "crude carbolic acid" can also be used. This serves mainly for the production of phenol, and consists of forty per cent. phenol, forty per cent. cresol, and twenty per cent. of the higher homologues of cresol, among which is mainly xylene. The carbolic acid can be treated in the same manner as stated for the production of the sulfonic acid from the waste product of the carbolic acid.

Naphtholsulfonic acid: (a) alpha-naphthol alpha sulfonic acid; (b) beta-naphthol beta sulfonic acid; (c) alpha-naphthol sulfonic acid, of Neville and Winther; (d) alpha-naphthol disulfonic acid, according to German patent No. 32,291; (e) alpha-naphthol trisulfonic acid, according to German patent No. 10,785; (f) beta-naphthol alpha monosulfonic acid; (g) beta-naphthol beta monosulfonic acid; (h) beta-naphthol alpha monosulfonic acid; (i) beta-naphthol alpha disulfonic acid; (k) beta-naphthol trisulfonic acid; (m) a mixture of the sulfonic acids mentioned under a and m in various quantities. These sulfonic acids are described by Schultz, *Chemistry of Coal Tar*, 1886, pp. 625, 646. They are formed by the reaction of sulfonic acid on the two naphthols, according to the concentration of the sulfuric acid, the temperature, and the duration of the reaction.

The lime salts are not very easily soluble in water, according to Beilstein, *Handbook of Organic Chemistry*, 1888, 2d Vol., pp. 561 to 570; but they are sufficiently soluble for the comparatively small quantities which are required for the bating liquors.

After the removal of the lime and cleaning the hides it is necessary to produce the swelling of the same, which is obtained by placing the hides in a liquor formed in the proportion of one to one thousand of a cresol sulfonic acid in water and leaving the hides for about twenty-four hours in this liquor; but even if the hides remain longer in the swelling liquor they would not be injured by the same. The swelling of the hides can be accomplished with a solution of sulfonic acid which is entirely free from or which is mixed with a small quantity of free sulfuric acid.

Generally speaking, the proportion of free sulfuric acid to the sulfonic-acid solution has to be adapted to the nature of the skins and to the purpose for which the latter are to be used. It may be added that for heavy hides which contain a considerable quantity of lime, and in which the hair is not removed before the bating operation, such cresol sulfonic acids can be used with advantage which contain, owing to their production, a considerable quantity of free sulfuric acid, as the sulfuric acid removes, primarily, the lime adhering to the surface of the hides and opens, so to say, the way to the interior of the hide for the slower-acting sulfonic acid.

Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. The process herein described of removing lime from skins and hides, which consists in subjecting the hides or skins to the action of a solution of a cresol sulfonic acid in water until the lime is neutralized, substantially as set forth.

2. The process herein described of removing lime from skins and hides, which consists in subjecting the hides or skins to the action of a solution of a cresol sulfonic acid and free sulfuric acid in water until all the lime is neutralized, substantially as set forth.

3. The process herein described of removing lime from skins and hides and subsequently swelling the same, which consists in subjecting the skins or hides to the action of a solution of a cresol sulfonic acid in water until all the lime is neutralized, and then treating the skins or hides with a second weaker solution of a cresol sulfonic acid in water, substantially as set forth.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

WILHELM DIETERLE.

Witnesses:

ERNST DIETRICH,
PAUL DRESCHER.