

UNITED STATES PATENT OFFICE.

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MANUFACTURE OF LEATHER AND LEATHER-LIKE PRODUCTS.

1,066,231.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that we, WERNER SPALTEHOLZ and KURT HARING, both subjects of the German Emperor, and residents of Leipzig, Germany, with the post-office address Mozartstrasse 21, and Hersfeld, Hesse-Nassau, Germany, with the post-office address Dippelstrasse 4, respectively, have invented new and useful Improvements in the Manufacture of Leather and Leather-Like Products, of which the following is a specification.

This invention consists in a method to fill hides and skins with tanning material in a specific manner not used hitherto in the art of tanning and to introduce materials other than the known vegetable and mineral tanning agents hitherto used as the different agents containing tannic acid or the like or mineral salts.

It is well known that hides or skins may be dehydrated by treatment with alcohol and it was thought that they could be completely freed from the water contained therein by treating them repeatedly with alcohol beginning with weaker solutions and finishing by nearly absolute alcohol. Applicants have discovered that such dehydrated hides or skins are suitable to be filled with and to retain besides the ordinary tanning agents a great variety of materials not used hitherto in the art of tanning if these materials are applied in the right way, and that the products thus obtained have useful properties especially that they are absolutely water-proof, if materials are used, which are insoluble in water. The materials to be used must be insoluble in water, soluble in a fluid which easily evaporates, as alcohol or benzol, turpentine, carbon disulfid (CS_2), they are applied to the hides or skins in such solutions and they must be left after the evaporation of the fluid in a non-crystalline shape. Such materials are in the first line materials having an asphaltic base, such as natural asphalt or artificial asphalt, resins as colophony or shellac, caoutchouc, gutta-percha, tar oils. These materials may be mixed with one another or be mixed with one or several of the following softening materials: paraffin, ceresin, linseed oil, vaseline, fats in order to render the products more subtle and less

brittle. Artificial asphalts may be obtained by distilling petroleum and treating the distillation residue with concentrated sulfuric acid, the treatment being carried on under a blast of air or oxygen. Such artificial asphalts have the property of being readily soluble in hydrocarbons and although any suitable artificial asphalt may be used in our process, we prefer to use those which possess this property to a high degree. The method of impregnating the said materials into the hides or skins dehydrated in the described way consists in placing the hides in solutions of these materials in one of the above said dissolving agents, preferably alcohol or benzol, for an appropriate time, removing the same from the solution and evaporating the dissolving fluid.

The invention further consists in an improvement of the preliminary dehydrating of the hides or skins by alcohol.

In recovering the alcohol by evaporation at atmospheric pressure, it appears that the leather suffers from the heat. By evaporating in a vacuum, not only is this objection removed, but, most unexpectedly it is found that the skin after its sojourn in the still is much more pliable and porous than if simply dried in the air. The certainty of uniformly tanning throughout is thereby increased. The reason for this is the somewhat surprising fact which has been discovered, namely that the evaporation in a vacuum removes more water from the skin than would be anticipated after the complete saturation with alcohol. It has always been assumed that the hide-substance of the prepared hide saturated with water, would part with the whole of this water if treated with alcohol so as to displace the water thereby. If for example after the last saturation the alcohol in which the hide was immersed acquired a strength of 92 per cent. by weight, it might be expected that the hide was saturated throughout with alcohol of this strength. On evaporating the alcohol from the hide in a vacuum, however, it was found that although the first portion of the distillate was alcohol of 92 per cent. strength, the percentage of alcohol gradually sank, more rapidly toward the end of the process, to between 60 and 70 per cent. The distillate contained

considerably more water than it should if the whole liquid had consisted of alcohol of 92 per cent. strength.

The skins prepared in the usual manner by liming or sweating, particularly if hide-butts (which are rectangular pieces cut from the center of the hide) are being tanned, are stretched on frames and then placed in the alcoholic liquid which contains 40 to 50 per cent. of alcohol, and are removed after 24-48 hours. They are then placed, for about the same time successively in mixtures of alcohol and water of 60, 70, 80, 90 and 96 per cent. strength, whereby chiefly in the 96 per cent. alcohol only a slight increase in the amount of water is observed. The hides saturated with alcohol are then introduced into a vacuum still and the alcohol is distilled off at a pressure of 120 m. m. decreasing to 5 m. m. toward the end of the distillation. This gradual decrease of the pressure is to keep the boiling point of the alcohol always at about the same temperature, the alcohol passing over toward the end of the distillation containing much more water than that passing over at the beginning. When maintaining these conditions the boiling point varies between 32 and 40-45° C. The proportion by weight of the alcohol to hide substance in the prepared hide is generally on the average, 50-55 parts of alcohol to 1-1.1 of prepared hide. Moreover, by the distillation, a further 10 parts of water are removed which would remain if the hide were dried in the air. In general the weight of the dry hide is 40 per cent. of the wet prepared hide. Of the alcohol in the hide about 5 per cent. is generally lost; the rest however is recovered. The figures given in respect of the hide vary naturally within certain limits, because as is known the hides of various animals have different absorptive capacities.

We will now describe some examples for the second step of our process.

The dry hide or skin is put in a solution of two parts of natural asphaltum and one part of artificial asphaltum in six parts benzol and remains therein for eight to fourteen days, to enable the solution to completely permeate the hide or skin. In special cases this object may be accomplished even in one day. Then the hide or skin is taken out of the bath cleansed with pure benzol and the benzol distilled off at atmospheric pressure, the temperature of such distillation not impairing the quality of the finished product. The product is subjected to the usual rolling or hammering and may then be used as sole leather. Good results may be obtained with a solution of one part of colophony and one part ceresin or paraffin in two parts of benzol, or ten parts of colophony and one part of caoutchouc or

guttapercha in twenty parts of benzol. These solutions may contain any dyestuff, which will dye the product throughout. The product containing caoutchouc may be vulcanized by a process in which sulfur chlorid may be used. By the proper mixture of the different materials products of different properties may be obtained.

Now what we claim and desire to secure by Letters Patent is the following:

1. The process of dehydrating hides or skins, which consists in treating a hide or skin with alcohol to form a mixture of alcohol and water with the water in the hide or skin, and subsequently removing said mixture from the hide or skin by distillation in a vacuum.

2. The process of dehydrating hides or skins which consists in treating a hide or skin successively with alcoholic solutions of gradually increasing percentages of alcohol, and subsequently removing the solution retained by the hide or skin by the distillation thereof in a vacuum.

3. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution of a material insoluble in water and forming a non-crystalline deposit after evaporation of the dissolving fluid.

4. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution of a mixture of materials, which are insoluble in water, form a non-crystalline deposit after evaporation of the dissolving fluid, one of the mixed materials forming a hard deposit and the other one a softer deposit.

5. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution of a mixture of materials, which are insoluble in water, form a non-crystalline deposit after evaporation of the dissolving fluid, one of the mixed materials forming a hard deposit and the other one being caoutchouc or guttapercha.

6. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution of a mixture of materials, which are insoluble in water, form a non-crystalline deposit after evaporation of the dissolving fluid, one of the mixed materials forming a hard deposit and the other one being caoutchouc or guttapercha and vulcanizing the same afterward.

7. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution in benzol of a material which is insoluble in water and will form a non-crystalline deposit upon the evaporation of the benzol.

8. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution comprising a suitable artificial asphalt.

9. The process of manufacturing products like leather which consists in dehydrating the hides or skins and treating the same with a solution comprising a suitable artificial asphalt mixed with natural asphalt.

10. As a new product of manufacture a hide or skin freed of its water and containing artificial asphalt.

11. As a new product of manufacture a hide or skin freed of its water and containing natural and artificial asphalt.

In testimony that we claim the foregoing as our invention, we have signed our names in presence of two witnesses, this 5th day of February, 1912.

WERNER SPALTEHOLZ.
KURT HARING.

Witnesses:

RUDOLPH FRICKE,
EMIL ROTH.