(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 324 734 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **03.04.91 Bulletin 91/14**

(51) Int. Cl.[5]: **C14C 9/00**, C14C 11/00

(21) Application number: **87902692.0**

(22) Date of filing: **13.04.87**

(86) International application number: **PCT/IT87/00034**

(87) International publication number: **WO 88/03958 02.06.88 Gazette 88/12**

(54) **A PROCESS FOR THE PRODUCTION OF LEATHER INTENDED FOR MAKING UPPERS OF FOOTWEARS AND THE PRODUCT THEREOF.**

(30) Priority: **18.11.86 IT 4866686**

(43) Date of publication of application: **26.07.89 Bulletin 89/30**

(45) Publication of the grant of the patent: **03.04.91 Bulletin 91/14**

(84) Designated Contracting States: **AT BE CH DE FR GB LI LU NL SE**

(56) References cited:
Chemical Abstracts, volume 86, no. 24, 13 June 1977, (Columbus, Ohio, US), W. Pauckner: "Incorporation of polymers into leather", see page 92, abstract 173097r, Rev. Tech. Ind. Cuir 1977, 69 (2), 42-50

(56) References cited:
Chemical Abstracts, volume 102, no. 20, 20 May 1985, (Columbus, Ohio, US), see page 109, abstract 168647q, & JP, A, 59226100 (IMAI, YASUO) 19 December 1984
US, A, 3843320 (S.H. Feairheller et al.) 22 October 1974

(73) Proprietor: **LUCIANI, Antonio**
Via Penne, 68
I-66013 Chieti (IT)

(72) Inventor: **LUCIANI, Antonio**
Via Penne, 68
I-66013 Chieti (IT)

(74) Representative: **de Simone, Domenico et al**
Ing. Barzanò & Zanardo Roma S.p.A. Via Piemonte 26
I-00187 Roma (IT)

EP 0 324 734 B1

Description

The present invention relates to a process for the production of leather intended for making uppers of footwears as well as to the products thereof. More particularly, the present invention relates to a process for treating wool-bearing sheep skins in order to obtain punctured or pierced leather having the compactness and strength features which are needed to employ the same for making footwear uppers having wool on their inner surface, said uppers being intended for footwears to be worn during the spring-summer period.

Such process distinguishes with respect to the traditional operations performed on wool-bearing sheep skins by the operations of treating said skins with acrylic and methacrylic resins respectively after the retanning and the puncturing steps.

Footwears are known at the present time which are suitable for hot months, more particularly for summertime, and employ pierced or punctured uppers obtained from calfskin and unlined on their inside, which uppers have the compactness and strength features required for that specific employment.

However, such leather products show the drawback of being poorly hygienic because of the presence of the holes as well as of being quite uncomfortable as regards friction that inevitably arises between the inner surface of the upper and the skin of the foot and the unsatisfying heat exchange between the outside and the inside, said heat exchange being necessary for keeping in a reliable way the optimal temperature inside the footwear.

Otherwise, the solutions suggested in the prior art for leather intended for making footwears to be worn in summer involved generally the use of materials, such as cloth, which are capable of assuring perspiration, but such materials certainly cannot be suggested for a long lasting footwear which does not undergo a rapid deterioration because of the action of weather, of impacts or of other external stresses, and so on.

Thus, the need is clearly evident for leather intended to make footwear uppers for the hot season, which uppers though provided with punctures or holes do not show the drawbacks mentioned above and allow in addition a footwear to be realized having the desired features of strength, durability and comfort.

In order to meet such requirement, the present invention suggests the employment, as the raw material for making uppers of summer footwears of punctured or pierced hides obtained from wool-bearing sheep skins, which are capable because of the presence of a wool layer on their inside surface to form a coating that is suitable because of its very nature to keep a constant inner temperature as well as to assure the circulation of air so avoiding overheating of feet and hence the sweating of the same, and, because of its intrinsic antistatic character, to reduce the introduction of dust. Moreover, the leather suggested according to the present invention has the characteristic property of giving rise to no compression areas localized at any part of the foot so that a uniform comfort is assured and the leather in question finally shows advantageously suitable as a stimulator of the peripheral circulation of blood and useful as an agent capable of absorbing the electrostatic energy built up in the body.

However, in order to exploit a raw material consisting of wool-bearing sheep skins, it is impossible to leave some of its original features out of consideration, such as for instance the characteristic of having a quite open fibrous texture because of the large amount of hair and also the presence of very short fibers that make such material unsuitable per se for use as uppers for footwears.

As a consequence, if order to allow a pierced or punctured leather product suitable for spring-summer footwears to be realized starting from wool-bearing sheep skins, the present invention suggests to perform acrylic and methacrylic resin treatment operations respectively at the end of the retanning step and after the puncturing or piercing step.

Indeed by means of such operations, the double object is obtained of :

a) giving the skins a higher compactness and strength so that the skin can be next punctured or pierced with no risks of tearing the same and the upper can be made by adapting the same to the desired model;

b) increasing the strength of the skin at the points corresponding to the inner surfaces of the holes so as to avoid the dilation of the same and the tearing of the skin as much as possible at the points corresponding to said surfaces during wear.

As already mentioned above, the basis operations of the process according to the present invention consist in the application and the subsequent two-stage polymerization of an acrylic resin inside the fibrous texture of the skin and in the application and subsequent polymerization of a methacrylic resin at points corresponding to the inner surfaces of the holes or punctures during a tanning treatment with retanning and finishing according to the procedure of the traditional type.

The traditional flowsheet of treatment of the skins normally provides different steps of working in a bath as well as different steps of dry working.

More precisely, the traditional work performed in a bath proceeds according to the following successive operational steps :

a) the soaking step wherein hides are deprived of the organic residual matter and blood and are softened, in order to avoid the need for succesive working of the fibers of the grain, by means of a bath that is made up of cool water and a surface active agent such as FORYLL BB (a mixture of imbibition agents, both anionic and non ionic, commercially available from the Henkel Company), the hides being then taken again to their natural concentration of water during the action of an enzyme product (an enzyme based product obtained from pancreatic bacteria) such as REVERDASE 120 (Rohne Poulenc) ;

b) the fleshing step wherein the shreds of flesh and the lumps of fat remaining after the skinning operation are removed, the subcutaneous layer being also removed so that the tanning products are allowed to penetrate the hide in a more uniform and rapid way ;

c) the washing step wherein the remaining dirt and a part of the natural fats which are present are removed from the hides, the natural fats remaining after this step becoming distributed in a more uniform way ; this step being performed employing preferably emulsified perchloroethylene which speeds the treatment up ;

d) the pickling step which represents the step of transition from the biological to the anabiological state, in which operation hides are prepared to be chrome tanned by making them more suitable to be passed through by chromium salts ;

e) the tanning step wherein the traditional treatment with a chromium salt is performed (basic chromium sulfate, pH 2.B) so as to obtain hides which are both soft and sufficiently compact and poorly elastic, and capable of allowing perspiration to occur ;

f) the acid removal step, wherein after the tanning maturation period with about 48 hours rest on the beam, the hydrolyzable acid bound to the protein substance is neutralized (as such acid causes non-uniform dyeing) by means of a compound consisting of a mixture of buffer salts exerting a neutralizing action (for instance, the CORATIL ND available from the Henkel) ;

g) the retanning step wherein the hides are given more strength and body, as well as a better adaptability to fluffing, and so on.

The dry working of the traditional type is based on the contrary on the operational steps of finishing, puncturing or piercing and the successive finishing.

According to the present invention, such working steps become integrated with the two steps already mentioned above in which the treatment with acrylic resins is performed.

More particularly, during the retanning step and, more precisely, in the final part of the retanning operation, in order to obtain the strengthening of the fibrous structure recourse is made to the employment of an acrylic type resin, more precisely to an acrylic ester which, when is incorporated in the fibers and becomes polymerized causes the fiber lattice to become thicker so as to give the hides, in addition to a higher compactness and strength, also the strength required for the successive piercing or puncturing operation.

The second operation which is characteristic of the process according to the present invention is performed during the dry working, after the piercing or puncturing step and it consists in treating the exposed surface of the hide, inside the holes, with methacrylic resin in order to increase the surface strength of the hide at the points corresponding to the inner walls of the holes, so as to avoid as much as possible the risk of dilating and tearing the hide during employed.

Accordingly, a specific object of the present invention is a process for the production of leather intended for making the uppers of footwears to be worn during the spring summer period wherein the wool bearing sheep skin is bath worked and then dry worked, wherein said bath working comprises the steps of leaking, fleshing, washing, pickling, tanning, acid removing and retanning and wherein said dry working comprises a first finnishing step ; a piercing or puncturing step and a second finishing step, characterized in that in the final part of the retanning step the skin are treated with an acrylic ester based resin in water solution and then said resin is made to polymerize so as to cause the original fibber lattice to become thicker and in that after said piercing or puncturing step, the skins are treated with a methacrylic resin in water solution and then said resin is polymerized at the point corresponding to the inner surface of the holes.

The choice of the type of acrylic polymer suggested in the present invention for the final phase of the retanning operation shows interesting and innovative if a comparison is made with resin of the melamine type, or of the ureic, diciandiamide, polyurethane and oleomaleic types which are traditionally employed for that operation.

Indeed, it is well known that some of said resins and more particularly the plolyurethane and oleomaleic resins, which are the most commonly employed, do not succeed in giving the hides a sufficient degree of compactness and strength.

The melamine and the ureic resins also have to be excluded because of the same reason, though such resins show the advantage of giving the hides quite good properties of feel and softness.

The resins of the dicyandiamide type, that on the contrary could give the desired properties of strength, are unsuitable to satisfy the objects of the present invention as they spoil at a remarkable extent the characteristics of the chrome tanning step and, above all the adaptability of the hides to the dyeing step.

The suggestion of the present invention consisting in the employment of acrylic resins in the form of water solutions and not in the form of water dispersions aims at obtaining a better and fuller penetration into the hide instead of obtaining just a surface deposition which might cause the product to become excessively hard, and, in addition, such suggestion allows the yield of the anionic dyes for leather employed to be increased reliably.

In the process according to the present invention, the acrylic ester polymeric compound is added to a neutralization bath consisting of water at 50° C and of an acid removal agent (for instance the CORATIL ND mentioned above), in which bath the hides have been dipped and adjusted to a pH of about 6.

It is interesting to observe that the employment of the neutralizing bath suggested according to the present invention, in addition to the effect of allowing the chromium to be fixed, also allows the acrylic ester polymeric compound employed in water solution to penetrate effectively, for instance ICATAN 38 of the Icap Company.

The acrylic ester resin is added preferably to the neutralization bath after about 1 hour, after the neutralization has occurred completely, at the concentration of 7 g/l, in order to give the possibilility of penetration into the hide fibers at a larger extent at the points where the hide itself is less strong and, more precisely, in the side parts where the structure is less relaxed and the fibers are longer.

Again according to the present invention the acrylic ester resin after a period ranging from 30 minutes to 2 hours, when the resin itself has completely gone into the hide, is caused to polymerize first with a slight addition of formic acid, so that the resin becomes bound to the fibers of the hide, and next it is caused to polymerize a second time in the dry state direct on the hides which now are completely dry, under a pressure of $19.62 \cdot 10^5$ Pa (20 kg/cm^2) and at a temperature of about 100-120°C for a period of 4-8 seconds.

After the piercing step of the wool-bearing hide, the piercing operation being performed by means of a press having a plate bearing small punches, the treatment with a methacrylic resin is carried out according to the procesure disclosed above

Preferably said treatment is performed by dipping the pierced hide into a water bath at 50-60°C in which a prepolymerized resin of methacrylic acid has been introduced (for example, DRASIL-ANG available from the Henkel Company) at the concentration of about 4-6 g/l and making the resin to polymerize definitively with the aid of the addition of formic acid for a period of about 30-45 minutes at a temperature of about 60°C.

Thus, the resin becomes deposited on the surface of the pierced hide at the points corresponding to the inner walls of the holes, where the resin itself becomes absorbed by the fibers uncovered as an effect of the piercing step, so that the advantageous effect, already mentioned above, of the increase in the surface strength of the hide is obtained.

The object of the present invention concerns also the hides obtained by means of the process mentioned above.

The present invention will be disclosed in the following just for exemplification and not for limitative purposes with reference to the enclosed drawings wherein :

Figure 1 is a block diagram of the process according to the present invention, and

Figure 2 is a schematic perspective view of a shoe realized employing leather obtained according to the present invention.

With particular reference to Figure 1, it is possible to observe the various operational steps for the treatment of a wool-bearing sheep skin, such steps being devided into the group A wherein the steps are collected which are characteristic of the bath working, and the group B wherein the steps are collected which are characteristic of the dry working. The distinctive steps of the inventive teaching consist in two treatments with acrylic and methacrylic resin respectively, which take place during the final part of the retanning comprised in group A and after the piercing step of the group B.

In the group A, it is possible to distinguish a biological phase of the treatment, comprising the soaking step, the fleshing and the washing step, a transition step consisting in the pickling operation and an anabiological step comprising the tanning, acid removal and retanning operations.

The dry working (B) comprises the finishing, piercing, treatment with an methacrylic polymeric compound which is a feature of the invention, and the successive finishing step.

More particularly, the technology illustrated above and characteristic of the present invention can be summarized as follows :

a) a stock of sheep raw hides bearing wool is dipped into a cold water bath (one hide for each volume of 20 l of water), said bath containing FORYLL BB, a surface active agent commercially available from the Henkel Company, at the concentration of 1 g/l and, the whole bath is left standing overnight, and in the morning it is next washed with tap running water till water comes out clean, then FORYLL BB (1 g/l) and REVERDASE 120 (0.2 g/l) are added, and the hides are left in the bath for 48 hours (the soaking step) ;

b) after the fleshing step, a bath is prepared consisting of water at 35-38°C and of 1.5 g/l of perchloroethylene (as the solvent) and 3 g/l of FORYLL BB (the surface active agent), and the hides are left dipped in such bath at the proportion of one hide for each 20 l ; then, the hides are washed with running

water ;

c) a cold water bath is prepared with addition of 40 g/l of salt (about 4° Bé) and the hides are left in such bath in the proportion of one hide for each 20 l of the bath for 30 minutes ; then, 2.5 g/l of an organic acid is added (for instance BASCAF F of the BASF Company) and the bath is left standing for 2 hours, adding next 3 g/l of formic acid and keeping the hides in the bath for 2-3 hours at pH 2.8 (the pickling step). Such pickling operation aims at preparing the hides to the chrome tanning step, making them more suitable to be passed through rapidly by the chromium salts which as a result of the acid character of the bath become less reactive so that consequently their penetration is more uniform. The addition of salt is necessary to avoid the swelling of the hides as an effect of the acid present ;

d) said hides are then treated as follows (the tanning step) :

2 hours in a bath of cold water (one hide for each 20 l) containing liquid chromium salt, the GRASSAN DHS commercially available form the Henkel Company is added in the proportion of 1,6 g/l, the bath is kept standing for 1 hour, then IMPLENAL AP commercially available from the BASF Company is added and the hides are kept in the bath for an additional hour, and finally 10 g/l of liquid chromium salt is added keeping the hides in said bath for 2 or 3 hours ; finally, 10 g/l of sodium carbonate and 1 g/l of sodium bicarbonate are added, keeping the hides dipped in the bath for 3-4 hours ; next the hides are spread out on a beam.

The procedure carried out in that way allows leather to be prepared suitable for making uppers of footwears as hides are obtained that are well tanned having a temperature Tg of about 90°C, and that are soft, with a rubber-like feel and sufficiently compact and poorly elastic in addition to be able to allow perspiration to occur freely.

Indeed, it can be observed that, in addition to the basic chromium sulfate added at a pH of about 2.8 which makes a uniform penetration easier, also a synthetic sulfite fat which is stable to electrolytes (GRASSAN DHS) as well as a masking agent (IMPLENAL AP) which shows a filling and stabilizing action of the chrome tanning are added. The last addition of an alkaline compound in the final step serves the purpose of making the chromium compound molecule larger and of fixing the same to the hide between its fibers so as to obtain a well tanned hide that shows strong and firm ;

e) in the acid removal step that is carried out after the maturation of the tanned hides by a rest period of about 48 hours on a beam, a bath of water at 45°C is employed, in which bath said hides are dipped (at the proportion of one hide for each 20 l of water) ; then, 2 g/l of CORATIL ND is added, the treatment being performed for 1 hour, then 3 g/l of GRASSAN DHS is added, the treatment being carried out for an additional hour ;

f) the retanning step is completed after carrying out the retanning step according to the traditional procedure, by inserting a treatment with an acrylic resin, such treatment being a characteristic feature of the present invention ; as a matter of practice, hides are treated in a bath of water at 45-50°C (in the proportion of one hide for each 8 l of water) containing 7.8 g/l of CORATIL ND and 7 g/l of ICATAN 38.

After the fluffing operations of the flesh side of the hides and after the dyeing of the hides by previously drying the same, the dry working step is performed ;

g) after the traditional finishing operation by previously applyins to the hide a water dispersion of an aliphatic-polyurethane (Astacin Finish PUD) in the proportion of 80-100 g/hide at 110°C and 151,95 bar (150 atm) with the consequent formation of a polymeric coating, the puncturing or piercing operation is carried out. The second step which forms a characteristic feature of the present invention occurs by dipping the hide in a bath of water kept at 50-60°C containing DRASIL-ANG available from the Henkel Company, which is a prepolymerized methacrylic resin in water solution, at the concentration of 4-6 g/l. Then, formic acid is added at 60°C over a period of 45 minutes and the polymerization is completed with the formation of a deposit on the surface of the pierced or punctured hide at points corresponding to the inner parts of the holes (h) and a further finishing (i) is performed.

Figure 2 shows an application of the leather obtained according to the present invention for the production of the upper of a footwear ; the wool layer 1 can be seen on the inner side of the footwear, while the velvet leather or the napped leather 2 provided with holes 3 can be seen on the outer part of the same.

The results are reported in the following of some standard tests carried out for the determination of the properties that are asked of leather intended for the production of uppers of footwears.

The tests performed on a specimen of ram skin after treating the same according to the present invention (specimen A) and on a specimen (B) of an untreated ram skin, are as follows :

determination of the tensile and elongation strength ;

determination of the tear resistance ;

determination of the stretching and of the tensile strength of the grain of leather by the method of the ball;

determination of wear resistance by repeated continuous folding of light leather and of their surface sizing.

Specimen A (treated according to the invention)

Standard procedure : UNI ISO 3376 – determination of the tensile and stretching strength.

The specimens opportunely conditioned undergo a tensile stress to failure on a tensile test device.

The tensile strength is obtained dividing the breaking or failure load by the cross section area of the specimen and is given as N/mm^2.

The ultimate elongation is calculated by the difference between the initial length of the specimen and its ultimate length. Such difference is expressed as the percentage with respect to the initial length of the specimen.

Conditioning and testing : Normal atmosphere, Al type (20 ± 2°C 65 ± R.H.).

– UNI 150 2589 – leather – mechanical tests – determination of thickness

Specimen	Tensile strength (N/mm^2)	ultimate elongation, %
1	11.4	39.4 %
2	12.35	42.2 %
3	12.52	44.0 %

Average tensile strength = 12.1 N/mm^2.

Average ultimate elongation, % = 41.87 %

Standard procedure UNI ISO 3377 IUP 8 – determination of tearing strength.

A rectangular specimen in which a slit has been out of the prescribed shape is hooked on the protruding ends of a pair of specimen holders fastened between the clamps of a tensile test device. The maximum elongation stress required for causing said specimen holders to separate is considered as the value of the tearing strength.

Conditioning and testing : Normal atmosphere, A2 type (23 ± 2°C 50 ± 5% R.H.).

Pulling speed : 100 ± 10mm/minute

Specimen	Tearing strength (N/mm)
1	51.6
2	44.5
3	42.3

Average tearing strength = 46.12 N/mm

Standard procedure UNI ISO 3379 – determination of stretching and of tensile strength of leather grain – the ball method.

A steel ball is pressed onto the central part of the flesh side of a leather specimen cut in the shape of a disk which is firmly fastened along its peripheral part.

The ball pressure and the consequent stretching of the specimen are recorded at the very moment when the leather grain becomes cracked and bursting of leather (possibly) occurs.

Conditioning and testing : normal atmosphere, A1 type (20 ± 2°C 65 ± 5% U.R.).

Specimen	1	2	3
crack formation load (N)	137.2	303.8	250.8
cracking strength (mm)	5.4	6.1	6.0
bursting strength (N)	470.4	678.1	527.2
stretching at bursting (mm)	7.2	9.3	8.6

Average crack formation load : 230.6 N

Average stretching at crack formation : 5.8 mm

Average bursting load : 558.6 N

Average stretching at bursting : 8.3 mm

Standard procedure : UNI 8433/TUP 20 – determination of repeated employment resistance (the employment consisting in continuous folding) of light leather and leather surface sizing.

Such determination is performed by clamping each specimen to the two terminals of the testing apparatus. One of the two clamping terminals is kept stationary while the other one is caused to oscillate with 22.5° amplitude at the frequency of 100 + 5 cycles/minute, so carrying with itself the folded specimen.

– Conditioning and testing : normal atmosphere of A1 type (20°C + 2°C 65 ± 5% R.H.).

– 6 rectangular specimens, size 70 × 45 mm, obtained by shearing. Number of test cycles : 50,000 cycles.

The specimens at the end off the test do not show any cracks or any other deterioration marks.

Specimen B (the untreated specimen)

Standard procedure : UNI ISO 3376 – determination of the tensile and elongation strength.

The specimens undergo after conditioning a tensile stress till failure on a tensile strength test machine.

The tensile strength is calculated by dividing the ultimate tensile load by the cross section area of the specimen and is expressed as N/mm^2.

The ultimate elongation is obtained by calculating the difference between the initial length of the specimen and its ultimate length. Such difference is expressed as the percentage with respect to the initial length of the specimen.

Conditioning and testing : normal atmosphere of the A1 type (20 ± 2°C 65 ± 5% R.H.).

– UNI ISO 2589 – leather – mechanical tests – determination of thickness

Specimens	Tensile strength (N/mm^2)	Ultimate elongation, %
1	21.28	60.6 %
2	19.7	46.8 %
3	15.96	45.6 %

Average tensile strength = 18.97 N/mm^2

Average ultimate elongation, % = 51.0 %

Standard procedure UNI ISO 3377 IUP 8 – determination of bearing strength.

A rectangular specimen in which a slit has been cut of the prescribed shape is hoocked on the protruding ends of a pair of specimen holders fastened between the clamps of a tensile test machine. The maximum elongation load required for causing the specimen holders to separate is considered as the tearing strength.

Conditioning and testing : normal atmosphere of the A2 type (23 ± 2°C 50 ± 5% R.H.).

Pulling speed : 100 ± mm/minute

Specimen	Tearing strength (N/mm)
1	73.1
2	68.6
3	64.1

Average tearing strength = 68.6 N/mm

Standard procedure UNI ISO 3379 – determination of the stretching and of the tensile strength of leather grain – the ball procedure.

A steel ball is pressed against the central part of the flesh side of a leather specimen cut in the shape of a disk and firmly fastened along its peripheral part.

The pressure of the steel ball and the stretching of the specimen are recorded at the very moment when the leather grain becomes cracked and the bursting (possibly) occurs.

Conditioning and testing : normal atmosphere of the A1 type (20 ± 2°C 65 ± 5% R.H.).

Specimen	1	2	3
crack formation load (N)	-	-	-
cracking strength (mm)	-	-	-
bursting load (N)	510.0	589.0	478.0
bursting stretch (mm)	10.5	9.2	9.0

Average bursting load : 528.6 N

Average bursting stretch : 9.5 mm

Standard procedure UNI 8433/IUP 20 – determination of the resistance to repeated employment (consisting in repeated continuous folding) of light leather and leather surface sizing.

Such determination is carried out by fastening each specimen to the two clamps of the testing apparatus.

One of the two clamps is kept stationary whereas the other one is made to oscillate with amplitude of 22.5° at the frequency of 100 ± 5 cycles/minute so carrying with itself the folded leather specimen.

– Conditioning and testing : normal atmosphere af the A1 type (20° ± 2°C 65 ± 5% R.H.).

– 6 rectangular specimen of sizes 70 × 45 mm obtained by shearing.

– Number of testing cycles 50,000 cycles.

The specimens at the end of the test do not show any cracks or other evidence of deterioration.

The following Table 1 summarizes the results of the technological tests mentioned above.

TABLE 1

Property	Specimen A (treated)	Specimen B (untreated)	Parameters of the ram skin	Parameters of the sheep skin
Average tensile strength	12.1 N/mm^2	18.97 N/mm^2	10	8
Elongation	41.87 %	51 %	40 %	40
Tearing strength	46.13	68.6	40	40
Average bursting load	558.6	528.6	120	120
Burst stretching	8.3	9.5	7.5	8
Average cracking load	230.6		120	120
Average cracking stretching	5.8	-	7.5	8
Bally test (50,000 flexions)	good	good		

It can be observed from such that the values obtained for the specimen A not only are better than those obtained with sheep skins intended for the production of uppers for footwears, but also are better than the results concerning ram skins.

The present invention has been disclosed with particular reference to some specific embodiments of the same, but it is to be understood that modifications and changes can be introduced in the invention without departing from the spirit and scope of the same for which an exclusive right is claimed.

Claims

1. A process for the production of leather intended for making the uppers of footwears to be worn during the spring summer period wherein the wool bearing sheep skin is bath worked and then dry worked, wherein said bath working comprises the steps of leaking fleshing, washing, pickling, tanning, acid removing and retanning and wherein said dry working comprises a first finishing step, a piercing or puncturing step and a second finishing step characterized in that in the final part of the retanning step the skin are treated with an acrylic ester based resin in water solution and then said resin is made to polymerize so as to cause the original fiber lattice to become thicker and in that after said piercing or puncturing step, the skins are treated with a methacrylic resin in water solution and then said resin is polymerized at the point corresponding to the inner surface of the holes.

2. A process according to claim 1 wherein the acrylic ester polymeric compound is added to a neutralization bath consisting of water at 50°C and of an acid removing agent, on which bath the skins are dipped and taken to a pH value of about 6.

3. A process according to claim 2 wherein the acrylic type resin is added to the neutralization bath after 1 hour when the neutralization is complete, till the concentration of 7 g/l.

4. A process according to claim 3 wherein the acrylic type resin, after a period ranging from 30 minutes to 2 hours, when the resin itself has completely penetrated into the skin, is caused to polymerized first with a slight addition of formic acid so that the resin becomes bound to the fibers of the skin, and next it is caused to polymerize a second time in the dry state, directly on the dry skin under a pressure of $19.62 \cdot 10^5$ Pa (20 kg/m^2) at a temperature of about 100-120°C for a period of 4 to 8 seconds.

5. A process according to anyone of claims 1 to 4, wherein the treatment with a methacrylic resin is carried out by dipping the pierced skin into a water hath kept at 50°-60°C in which a methacrylic resin has been introduced after previous polimerization of the same, its proportion in the bath being of about 4-6 g/l and then carring out the definitive polymerization of said methacrylic resin with the addition of formic acid for about 30-45' a temperature of about 60°C

6. Shep skins bearing wool on the inner side, intended for the production of spring-summer footwears uppers, said skin being obtained by the process claimed in anyone of the preceding claims 1-5.

7. A process for the production of leather intended for making uppers of footwears and the product thereof according to claims 1-7 substantially as disclosed and illustrated above.

Ansprüche

1. Verfahren zur Herstellung von Leder, die zur Ausarbeitung von Schaeften fuer die im Fruehling und Sommer anzuziehenden Schuhwerke in dem die noch Wolle tragenden Schaffellse zuerst einer Badbearbeitung und dann einer Truckenbearbeitung unterworfen werden, wobei die Badbearbeitung aus Einweichen, Entfleischen, Waschen, Pickeln, Gerben, Saeureentfernung und Nachgerben und die Trockenbearbeitung aus einer ersten Zurichtphase, einer Stanz- oder Lochphase und einer zweiten Zurichtphase bestehen, dadurch gekennzeichnet, dass im letzten Teil der Nachgerbenphase die Fellse mit einer Akryllesterharz-Wasserloesung behandelt werden, das Harz wird dann polymerisiert, um dadurch das urspruengliche Fasergitter dicker werden zu lassen und dass, nach der Stanz- oder Lochphase eine weitere Behandlung mit einer Methakrylharz-Wasserloesung durchgefuehrt wird, wonach dieses Harz wird an den Stellen polymerisiert, die den Innerflaechen der Loecher entsprechen.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die polymere Akrylesterverbindung einem Neutralisserungsbad zugegeben wird, das aus auf 50°C erhitztem Wasser und einem Saeureentfernungsmittel besteht und dass die Haeute in dieses Bad eingetaucht und bis zu einem pH-Wert von etwa 6 gehalten werden.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass das Akrylesterharz dem Neutralisierungsbad nach einer Stunde bis zur Konzentration von 7 g/l, zugegeben wird, nachdem die Neutralisierung abgeschlossen ist.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, dass das Akrylesterharz nach einer Zeitspanne von etwa 30 Minuten bis 2 Stunden, in der das Harz in die Haut vollstaendig eingedrungen ist, zur Polymerisation gebracht wird, zuerst durch die Zugabe einer kleinen Menge von Formsaeure, wodurch das Harz an die Fasern der Haut gebunden wird, und dass anschliessend das Harz im trockenen Zustand unter einem Druck von $19{,}62 \times 10^5$ Pa (20 kg/m^2) bei einer Temperatur von etwa 100-120°C in einer Zeitspanne von 4 bis 8 Sekunden das zweiste Mal zum Polymisieren gebracht wird.

5. Verfahren nach einem der Ansprueche 1 bis 4, dadurch gekennzeichnet, dass die Behandlung mit einem Methakrylharz durch Eintauchen der gestanzten Haut in ein auf 50-60°C erhitztes Wasserbad durchgefuehrt

wird, in das ein Methalkrylharz nach seiner vorherigen Polymerization in einer Menge von 4-6 g/l eingefuehrt wird, wonach das genannte Methakrylharz duch die Zugabe von Formsaeure in einer Zeitspanne von 30 bis 45 Minuten und bei einer Temperatur von etwa 60°C endgueltig zur Polymerization gebracht wird.

6. Schafshaeute mit Walle auf der Innenseite, die fuer die Herstellung von Schaeften fuer die im Fruehling und Sommer zu tragenden Schuhwerke, dadurch gekennzeichnet, dass die genannten Haeute nach dem in einem der vorhergehenden Anspruche beanspruchten Verfahren erhalten werden.

7. Verfahren fuer die Herstellung von Leder fuer die Fertigung von Schaeften fuer Schuhwerke und das damit erhaltene Produkt, nach den Anspruechen 1 bis 6, im wesentlichen wie hier oben beschrieben und veranschaulicht.

Revendications

1. Procédé pour la production de cuirs destinés à la préparation d'empeignes de chaussures à porter au printemps et en été, dans lequel la peau de mouton avec la laine est ouvragée à bain et ensuite à sec, l'ouvrage à bain comprenant l'assouplissement, l'écharnage, le lavage, le picklage, le tannage, la désacidification et le retannage, et l'ouvrage à sec comprenant la première phase de finissage, la phase de perforation ou perçage et la deuxième phase de finissage, caractérisé en ce que la peau est traitée avec une résine d'ester acrylique en solution aqueuse et ensuite laditte résine est faite polymériser de façon à rendre plus épais le réseau des fibres et en ce que après laditte phase de perforation ou perçage,les peaux sont traitées avec une résine methacrylique en solution aqueuse et ensuite laditte résine est polymérisée aux points correspondants à la surface intérieure des trous.

2. Procédé selon la revendication 1, caractérisé en ce que la composition polymérique d'ester acrylique est ajoutée au bain de neutralisation consistant d'eau à 50°C et d'un agent de désacidification, les peaux étant plongées dans ledit bain et tenues jusqu'à ce que elles atteignent un valeur pH à peu près de 6.

3. Procédé selon la revendication 2, caractérisé en ce que la résine acrylique est ajoutée au bain de neutralisation après 1 heure, quand la neutralisation est complétée, jusqu'à la concentration de 7 g/l.

4. Procédé selon la revendication 3, caractérisé en ce que la résine acrylique, après une periode de 30 minutes à 2 heures, quand la résine est complètement pénétrée dans la peau, est polymérisée au début par l'addition d'une petite quantité d'acide formique de façon que la résine devient liée aux fibres de la peau, et ensuite elle est faite polimérisée une deuxième fois à l'état sec directement sur la peau sèche sous une pression de $19{,}62.10^5$ Pa ($20 kg/m^2$) à une température à peu près de 100-120°C pendant une période de 4 à 8 secondes.

5. Procédé selon une quelconque des revendication 1-4, caractérisé en ce que le traitement avec une résine methacrylique est réalisé par le plongement de la peau perforée dans un bain d'eau à la température de 50-60°C, dans lequel une résine methacrylique était introduite après sa polymérisation, la proportion de laditte résine dans le bain étant à peu près de 4 g/l, et en ce que ensuite laditte résine methacrylique est polymérisée par l'addition d'acide formique à peu près en 30-45 secondes à la température de 60°C ca.

6. Peau de mouton avec la laine pour la production d'empeignes de chaussures à porter au printemps et en été, laditte peau étant obtenue par le procédé revendiqué dans une quelconque des revendications 1-5.

7. Procédé pour la production de peaux pour les empeignes de chaussures et le produit obtenu selon les revendications 1-6, fondamentalement comme décrit et illustré ci-dessus.

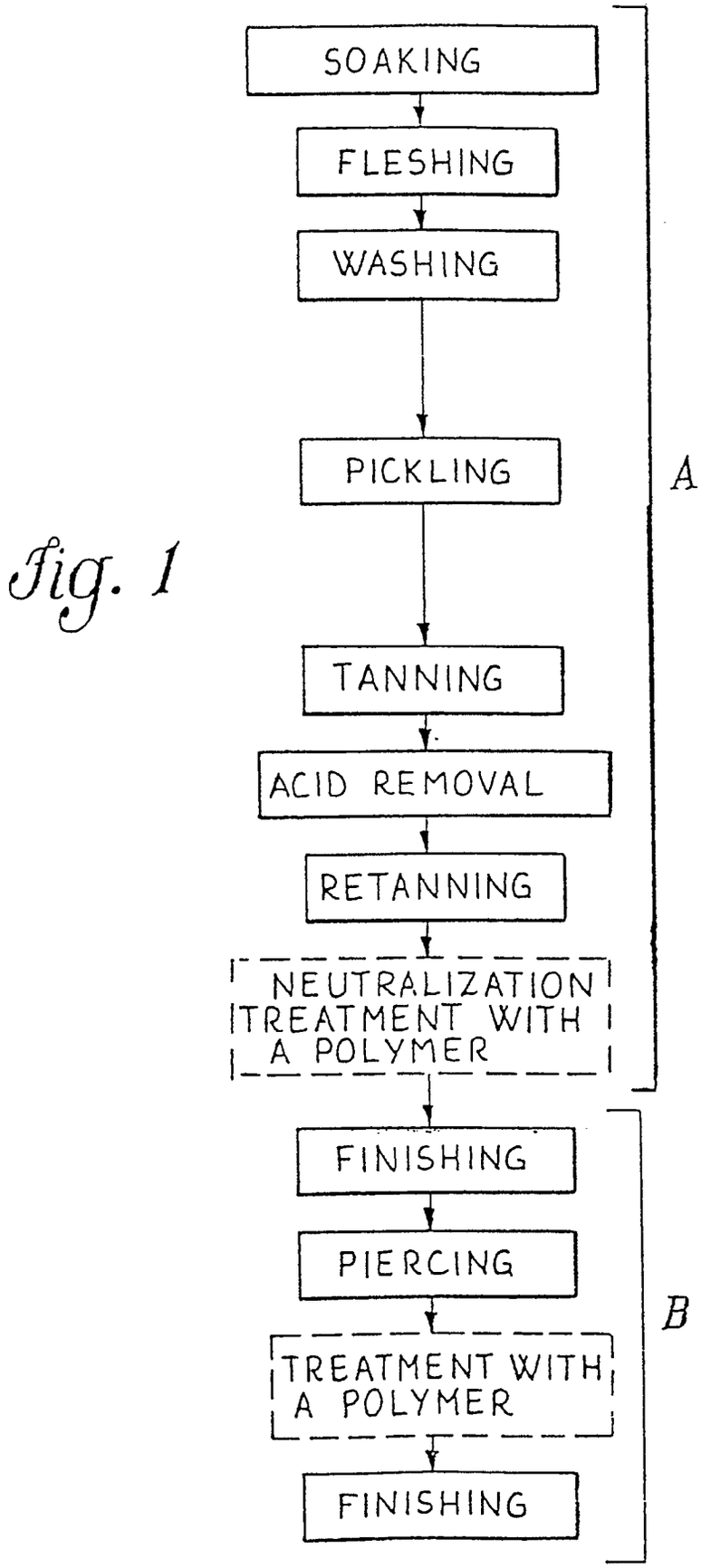
SOAKING
FLESHING
WASHING
PICKLING
TANNING
ACID REMOVAL
RETANNING
NEUTRALIZATION TREATMENT WITH A POLYMER
FINISHING
PIERCING
TREATMENT WITH A POLYMER
FINISHING
A
B

Fig. 1