Abstract:
The present invention relates to a method for the treatment of a semimanufactured product made of leather or similar material. The method comprises the steps of: providing the semimanufactured product to be treated; preparing a treatment solution comprising a binder solution and silver in granules; applying the treatment solution to at least one surface of said semimanufactured product to be treated. The binder solution comprises natural proteins in aqueous solution. The present invention also relates to an item produced from a semimanufactured product made of leather or similar material treated with the aforesaid method.
The present invention relates to a method for the treatment of a semimanufactured product made of leather or similar material, and an item made from a semimanufactured product treated according to such a method.

The present invention is targeted in particular at the processing of leather or imitation leather to be used to produce items destined to come at least partly into contact with the skin of an end user. Possible examples of these items are articles of clothing (jackets, coats), footwear, watchstraps, small leather items (bags and parts thereof, wallets), coverings for objects of various nature, such as coverings for eyewear, seat coverings (i.e. for automobiles), or the like. Naturally, this list is provided by way of non-limiting example.

One of the requirements related to the use of hide, leather and imitation leather in similar products is that of ensuring a high degree of comfort for the user. Not only must the leathers be soft and
comfortable, but they must also ensure a high degree of water vapour permeability, so that when the leather is in contact with human skin, the perspiration produced by the user does not cause an unpleasant feeling when the item is worn.

A further requirement is that of limiting the production of unpleasant odours caused by perspiration produced by the user. This requirement is particularly important in the footwear sector, where unpleasant odours frequently occur due to perspiring produced by the user's feet when wearing the footwear.

In order to overcome the aforesaid drawbacks, it is known that silver has antiseptic, deodorant and antibacterial properties and that it is used for this purpose for example also in body deodorants.

In order to apply and fix silver in powder form to the leather various methods have been proposed.

For example, it has been proposed to bury the powdered silver in synthetic resins and then apply the resins to the leather. However, this solution has the drawback that synthetic resins form a relatively thick and heavy film on the leather which almost totally waterproofs the surface of the leather, consequently reducing breathability. The presence of
these films also reduces the natural look of the leather, which is therefore of low prestige from the point of view of merchandise.

It has also been proposed to bury the powdered silver in acrylic paints or in PVC, but this solution also has analogous drawbacks to those indicated above.

The use of synthetic chemical products also has the further drawback of the complexity of the disposal of production residues, with high environmental impact.

The problem underlying the present invention is therefore to provide a method for the treatment of leather (or of a similar material) that is able to at least partly overcome the drawbacks mentioned with reference to prior art.

In particular, the problem underlying the present invention is to provide a method for the treatment of leather or of similar materials capable of offering a high degree of comfort, and a high level of breathability and of reducing odours caused by perspiration produced by the user's skin.

A further objective of the present invention is to provide a method for the treatment of leather or similar materials with limited environmental impact.
These and other objects are achieved by a method for the treatment of a semimanufactured product made of leather or similar material according to claim 1 and by an item produced from a semimanufactured product made of leather or similar material produced according to this method in accordance with claim 30.

The dependent claims define possible advantageous embodiments of the method and of the item according to the invention.

To better understand the invention and the advantages thereof some non-limiting examples of embodiments are described below.

The method according to the present invention is aimed at the treatment of leathers, in particular leathers of various kinds, but can also be used to treat fabrics similar to leather, such as imitation leather. In the present description, reference will be made by way of example to hide and leather.

The method according to the invention firstly comprises a step to provide a semimanufactured product to be treated. This semimanufactured product can for example comprise a leather pre-tanned with known procedures.

Treatment of the semimanufactured product takes place through the application thereto, according to
procedures to be described, of a special treatment solution which is prepared according to specific procedures.

The treatment solution is not necessarily applied to the entire semimanufactured product, but preferably only to one surface thereof. In other words, only one side of the leather is treated with the method according to the invention. In this manner the treatment is limited to the portion of the leather destined to come into contact with the user's skin. For example, in the case of footwear, the treated surface is that destined to delimit the seat for the user's foot and which therefore will come into contact therewith. In the case of a watchstrap, the treated surface is the inner surface of the watchstrap, i.e. the surface that will come into contact with the skin of the user's wrist.

The treatment solution to be applied to the semimanufactured product includes a binder solution based on natural proteins in aqueous solution and silver in granules.

The natural proteins used in the binder solution can be of various type. Preferably, they are selected from the group consisting of casein, egg albumin, blood albumin.
The preferred binder used in the solution is in any case casein as this has the capacity to absorb moisture (which can, for example, derive from perspiration of the foot when the semimanufactured product is used to manufacture footwear). Casein is a phosphoprotein which can be obtained from milk through appropriate treatment processes (e.g.: pressure, fermentation, acidification).

Moreover, it is also eventually possible to use a mixture containing one or more of the natural proteins listed to give particular characteristics to the leather treated with the method according to the invention. For example, it is possible for the binder solution to be provided with a combination of casein with albumin. In fact, this combination allows a sufficiently shiny film to be obtained on the leather.

The binder solution can also comprise further additives suitable to give the leather specific characteristics. These additives can include one or more of the following additives: linseed mucilage, cellulose derivatives, such as carboxymethyl cellulose, gelatin, lac, soaps.

Linseed mucilages and cellulose derivatives give the films a high filling capacity on the leather.
Gelatin gives the leather a soft handle and pasty texture. Lac gives the leather shine and homogeneity.

Advantageously, the binder solution contains plasticizers suitable to reduce the stiffness, fragility and elasticity of the film of protein solution once this has been applied to the leather. The plasticizers are preferably selected from the group consisting of: sodium sulphoricinate, higher alcohols, glycols, glycerines, natural oils, natural waxes.

As natural oil it is possible, for example, to use medium sulfonation castor oil.

Natural waxes can be of animal or vegetable origin.

The vegetable waxes can be selected from a group consisting of: carnauba, which is extracted from the leaves of the Brazilian carnauba plant; montan, extracted from peat and lignite; candelilla, which is extracted mainly from the trunk of a Mexican plant.

Animal waxes can instead be selected from the group consisting of: secretions from insects, such as beeswax; secretions from sebaceous glands, such as lanolin; secretions extracted from the adipose tissues of mammals, such as the sperm whale or whale.

The application of natural proteins in aqueous
solution to the leather has many advantages.

Firstly, the absence of chemical solvents limits the overall environmental impact of the treatment. Moreover, the items produced from semimanufactured products treated with the method according to the invention ensure high ecological quality standards.

A further advantage linked to a binder solution of this type is that the presence of natural proteins ensures that the possibility of causing allergies in the end user is low.

A further advantage linked to the use of an aqueous binder solution is the possibility of producing very thin, transparent and shiny finishes, which allow the leather to retain its natural water vapour permeability, while offering a high degree of comfort. Moreover, the antiseptic properties of silver are increased by the fact that it is immersed in a vapour permeable substance.

Advantageously, the binder solution has anionic charge and, preferably, a pH of about 8. The percentage of casein in the binder solution is preferably between 6% and 12%, even more preferably equal to about 8%.

In accordance with an embodiment, the binder solution used is the solution called Hydrofin T®,
manufactured by S.I.C. International™.

The granules of silver of the treatment solution preferably comprise granules of pure or substantially pure silver. According to a possible embodiment, the granules of silver in the treatment solution have a grain size of less than or equal to 10 microns. Preferably, a part of the granules has a grain size of less than 10 microns. According to a possible embodiment, a part, preferably about 50%, of the granules of silver has a grain size of less than 7 microns.

Preparation of the treatment solution from the binder solution and from the granules of silver with the aforesaid properties comprises a series of successive steps.

The binder solution and the granules of silver are mixed, preferably in a ratio of 1:10 (i.e. with one part of powdered silver and ten parts of binder), dispersing the silver in the binder solution. The suspension thus obtained is then mixed until obtaining a substantially homogenous paste.

Preferably, water is subsequently added to the paste thus obtained, in such a way as to obtain a diluted solution. According to a preferred embodiment, water is added in a quantity such that in
the treatment solution the granules of silver reach a concentration of between 7 and 12 g/l, preferably equal to about 10 g/l.

Advantageously, the solution thus obtained is then kept under stirring, for example using a blade stirrer. The maintenance speed is preferably between 250 and 350 rpm, even more preferably equal to about 300 rpm.

Once the treatment solution has been prepared according to the procedures described, the treatment method includes a step to apply the treatment solution to the semimanufactured product to be treated, in particular to the surface destined to come into contact with the skin of the end user.

In accordance with a possible embodiment, the treatment solution is applied by spraying, preferably by means of compressed air guns. The spray pressure is preferably maintained between 0.4 and 0.7 atm. The use of these pressures ensures precision during application and also makes it possible to limit the phenomenon of bounce-back of the solution on the surface of the semimanufactured product. The quantity of treatment solution which is lost through bounce-back is therefore extremely low, to the advantage of production economy.
Preferably, the treatment solution is sprayed through nozzles having a diameter between 0.5 and 1.3 mm, even more preferably equal to about 0.8 mm. In other words, the treatment solution is applied at low pressure and high volume, with reference to the pressures and to the volumes which are normally used to treat leathers (for example, when applying dyes).

Preferably, the step to apply the treatment solution is performed automatically. In particular, the semimanufactured products are transported on a conveyor belt and, when each of them is in proximity of the spray guns, specific sensor means detect their presence in the correct position and then transmit suitable signals to a control processor which activates the spray guns, opening their nozzles.

Advantageously, the step to apply the treatment solution takes place according to a plurality of successive application operations. According to a possible embodiment, the treatment solution is applied in four subsequent application operations, each applying between 40 and 60 grams of treatment solution per square metre of surface of the semimanufactured product. Even more preferably, the quantity of treatment solution applied is equal to about 50 grams per square metre of surface of the
semimanufactured product. At the end of the four
application operations, the treatment solution
applied is therefore equal to about 200 g per square
metre of surface of semimanufactured product, which,
according to a preferred embodiment, corresponds to 2
grams of granules of silver per square metre of
semimanufactured product to be treated.

Advantageously, the treatment method according to
the invention also comprises a step to fix the
treatment solution to the surface of the
semimanufactured product. The fixing step has the
purpose of insolubilizing the natural proteins of the
binder solution, so as to make them swell less in
water and thus obtain stability to wet treatments.

Preferably, the fixing step takes place according
to a plurality of successive fixing operations. In
particular, each application operation is followed by
a fixing operation suitable to fix the treatment
solution applied in the specific application
operation to the surface of the semimanufactured
product. Preferably, the fixing operations are also
four in number, each following one of the four
application operations described previously.

According to a possible embodiment, each of the
fixing operations comprises the application of a
fixing substance to the surface of the semimanufactured product (to which the treatment solution has previously been applied).

Preferably, the fixing substance contains aldehydes suitable for crosslinking the natural proteins of the binder solution (and of the treatment solution). In particular, according to a preferred embodiment, the fixing substance contains glyoxal, which is suitable for crosslinking casein. Glyoxal is preferably included in the fixing substance in a percentage between 3% and 5%.

In accordance with an embodiment, the method according to the invention comprises a step to dry the semimanufactured product.

The drying step preferably includes a plurality of drying operations. In particular, the drying step includes a plurality of drying operations, each of which is performed subsequently to respective application operations, and a plurality of drying operations, each of which is performed subsequently to respective operations to fix the treatment solution on the semimanufactured product.

The single drying operations can be implemented by placing the semimanufactured product in an environment which has a predetermined drying
temperature, for example in a drying oven. The drying temperature is preferably between 30°C and 50°C, even more preferably equal to about 40°C. The time of the drying operations preferably varies from 20 to 40 seconds. In particular, the times of the drying operations are selected so that the operations to apply the treatment solution take place on the dry leather, while the fixing operations take place on the leather while it is still, albeit slightly, damp. In fact, in this manner the fixing substance is made to act in depth, instead of only on the outer surface of the leather. For this purpose, the drying operations subsequent to the application operations preferably have a duration of about 20 seconds, while the drying operations subsequent to the fixing operations preferably have a duration of about 40 seconds.

In accordance with an embodiment, the method according to the invention also comprises a final buffing step. This buffing step can, for example, be obtained through hot stretching using heated rollers that press the semimanufactured product on the treated side. This process allows a leather with a high level of smoothness and shine to be obtained.

The semimanufactured product treated according to
the procedures described can advantageously be used to manufacture a particular item, such as an article of clothing, footwear, a watchstrap, a small leather article (wallet, purse), a covering for objects (for eyewear, for seats), or the like.

For example, with reference to footwear, it is possible to treat the surface of the semimanufactured product destined to come into contact with the foot of the user with the method according to the invention.

Due to the treatment to which the semimanufactured product is subjected, based on an aqueous binder solution, the leather of the shoe is soft and elastic, as well as sufficiently breathable. Moreover, the presence of the granules of silver limits the production of unpleasant odours linked to perspiration of the foot due to the antiseptic, antibacterial and odour-preventing action of the silver dispersed on the internal surface of the shoe.

Analogous effects are naturally obtained also in other types of article destined to come into contact with the skin and possibly with the perspiration of the user.

From the above description those skilled in the art can appreciate how with the method according to
the invention it is possible to obtain leathers (or similar materials) and therefore items that ensure a high degree of well-being, both in terms of softness and comfort, and in terms of reducing unpleasant odours.

Moreover, those skilled in the art may appreciate how the use of natural proteins in the binder solution ensures a low environmental impact of the process, and reduces the risk of allergic reactions of the user.

As treatment of the semimanufactured product is performed using an aqueous solution without pigments and dyes, the leather has an extremely natural appearance.

Finally, those skilled in the art may appreciate how the combination of aqueous binder solution and powdered silver, especially when applied to leather, provides products with a high level of permeability to perspiration and the capacity to limit the occurrence of unpleasant odours.

For the purpose of satisfying specific contingent requirements, those skilled in the art will be able to make numerous modifications or additions to the embodiments described above of the method for the treatment of a semimanufactured product made of
leather or similar material and of the item produced with the semimanufactured product treated according to this method, or to substitute elements with other functionally equivalent elements, without however departing from the scope of the appended claims.

*** * ***
CLAIMS

1. A method for the treatment of a semimanufactured product made of leather or similar material, said method comprising the steps of:

- providing the semimanufactured product to be treated;
- preparing a treatment solution comprising a binder solution and silver in granules;
- applying said treatment solution to at least one surface of said semimanufactured product to be treated,

wherein said binder solution comprises natural proteins in aqueous solution.

2. The method according to claim 1, wherein said natural proteins comprise casein and/or egg albumin and/or blood albumin.

3. The method according to claim 1 or 2, wherein said binder solution comprises plasticizers of natural proteins, said plasticizers being selected from the group consisting of: sodium sulphoricinate, higher alcohols, glycols, glycerines, natural oils, animal waxes selected from the group consisting of secretions from insects, secretions from sebaceous glands, secretions extracted from the adipose tissues of mammals; vegetable waxes selected from the group
consisting of carnauba, montan, candelilla.

4. The method according to any one of the preceding claims, wherein said binder solution comprises further additives selected from the group consisting of: linseed mucilage, cellulose derivatives, gelatin, lac, soaps.

5. The method according to any one of the preceding claims, wherein said natural proteins are present in the binder solution with a percentage of about 8%.

6. The method according to any one of the preceding claims, wherein said binder solution has anionic charge and has a pH of about 8.

7. The method according to any one of the preceding claims, wherein said binder solution is the solution Hydrofin T™, manufactured by S.I.C. International™.

8. The method according to any one of the preceding claims, wherein the silver in granules has a grain size of less than or equal to 10 microns.

9. The method according to any one of the preceding claims, wherein about 50% of said granules of silver have a grain size of about 7 microns.

10. The method according to any one of the preceding claims, wherein said step to prepare the treatment solution comprises the steps of:

- providing the binder solution;
- providing the silver in granules;
- mixing the binder solution and the silver in granules;
- mixing the binder solution and the silver in granules until obtaining a substantially homogenous paste.

11. The method according to the preceding claim, wherein said step to prepare the treatment solution also comprises a step to add water to said paste.

12. The method according to the preceding claim, wherein the water is added in a quantity such that the silver in granules reaches a concentration of about 10 g/l.

13. The method according to any one of claims 10 to 12, wherein said step to prepare the treatment solution comprises a step to maintain said paste under stirring.

14. The method according to the preceding claim, wherein said step to maintain the treatment solution under stirring is performed using a stirrer moving at the speed of about 300 rpm.

15. The method according to any one of the preceding claims, wherein said step to apply the treatment solution to the semimanufactured product to be treated includes a step to spray said treatment
solution onto the surface of the semimanufactured product.

16. The method according to the preceding claim, wherein the treatment solution is sprayed onto the semimanufactured product at a pressure between 0.4 and 0.7 atm.

17. The method according to claim 15 or 16, wherein the treatment solution is sprayed through nozzles having a diameter of about 0.8 mm.

18. The method according to any one of the preceding claims, wherein said step to apply the treatment solution comprises a plurality of subsequent application operations of the treatment solution on the at least one surface of the semimanufactured product to be treated.

19. The method according to the preceding claim, wherein said step to apply the treatment solution to the semimanufactured product to be treated comprises four subsequent application operations of said plurality of subsequent application operations.

20. The method according to claim 18 or 19, wherein each of said application operations is such as to apply about 50 grams of treatment solution per square metre of said at least one surface of the semimanufactured product.
21. The method according to any one of the preceding claims, further comprising a step to fix the treatment solution applied to said at least one surface of the semimanufactured product to be treated.

22. The method according to the preceding claim when dependent on any one of claims 18 to 20, wherein said fixing step comprises a plurality of fixing operations, each fixing operation of said plurality of fixing operations being subsequent to an application operation of said plurality of application operations.

23. The method according to claim 21 or 22, wherein said fixing operations comprise the application to said at least one surface of the semimanufactured product of a fixing substance.

24. The method according to the preceding claim, wherein said fixing substance contains aldehydes suitable for crosslinking said natural proteins of the binder solution.

25. The method according to claim 23 or 24, wherein said fixing substance contains glyoxal, preferably included in a percentage between 3% and 5%.

26. The method according to any one of the preceding claims, further comprising a step to dry the
semimanufactured product.

27. The method according to the preceding claim, wherein said drying step includes a plurality of drying operations subsequent to respective application operations of said plurality of application operations and a plurality of drying operations subsequent to respective fixing operations of said plurality of fixing operations.

28. The method according to the preceding claim, wherein each of said drying operations includes a step to place the semimanufactured product to be treated in an environment at about 40°C for a time between 20 and 40 seconds.

29. The method according to any one of the preceding claims, comprising a buffing step, preferably by means of hot stretching.

30. An item produced from a semimanufactured product made of leather or similar material treated with the method according to any one of the preceding claims.

31. The item according to the preceding claim, wherein said at least one surface of the semimanufactured product to be treated is arranged in said item in a position such as to come into contact with the skin of the user of the item in conditions of use thereof.
### A. CLASSIFICATION OF SUBJECT MATTER

INV. C14C11/00 C14C13/00

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DATABASE WPI Week 200118 Thomson Scientific, London, GB; AN 2001-180520 XP002586402 &amp; RU 2 160 784 CI (LEATHER SHOE IND RES INST ENTERPRISE) 20 December 2000 (2000-12-20)</td>
<td>1-31</td>
</tr>
</tbody>
</table>

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

* Special categories of cited documents:
  - 'A' document defining the general state of the art which is not considered to be of particular relevance
  - 'E' earlier document but published on or after the international filing date
  - 'R' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - 'O' document referring to an oral disclosure, use, exhibition or other means
  - 'P' document published prior to the international filing date but later than the priority date claimed
  - 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  - 'S' document member of the same patent family

Date of the actual completion of the international search: 28 June 2010

Date of mailing of the international search report: 05/07/2010

Name and mailing address of the ISA:

European Patent Office, P.B. 5818 Patentlaan 2 N.L.; 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer: Neugebauer, Ute
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 5 531 795 A (RASMUSSEN LARS [DK] ET AL) 2 July 1996 (1996-07-02) column 1, line 11 - column 4; example 1</td>
<td>1-31</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>JP 2006089583 A</td>
<td>06-04-2006</td>
<td>NONE</td>
</tr>
<tr>
<td>RU 2160784 CI</td>
<td>20-12-2000</td>
<td>NONE</td>
</tr>
<tr>
<td>US 5531795 A</td>
<td>02-07-1996</td>
<td>AU 665298 B2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 5693994 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR 9307611 A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69324039 D1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69324039 T2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DK 673441 T3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0673441 A1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2131665 T3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GR 3030321 T3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 8504453 T</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NZ 258866 A</td>
</tr>
<tr>
<td>KR 20060000291 A</td>
<td>06-01-2006</td>
<td>NONE</td>
</tr>
</tbody>
</table>