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(54) **CHROMIUM ENHANCED TANNING PROCESS**

(57) The invention concerns a process for tanning a hide to obtain leather comprising the following steps:

- a) a pickling step with acid and salt,
- b) a tanning step with an ololation agent

c) a basification step,
wherein in step b) an electric field is produced, by placing the hide between the two electrically powered electrodes.

EP 3 527 675 A1

Description**FIELD OF THE INVENTION**

[0001] The present invention is related to an enhanced process of tanning hide to obtain leather, reducing significantly the time necessary to produce the final leather, while reducing the volume of bath and increasing the possibility to use different chemicals as olating agents with respect to the metal salts, leading consequently to a reduced environmental impact.

STATE OF THE ART

[0002] Hide tanning is a process in which the collagen protein present therein reacts with tanning agents, originating leather. The tanning process is therefore one of the essential steps in leather production process. It is a very old process, whose purpose is to avoid hide degradation and putrefaction, by means of a protein crosslinking phenomenon caused by the action of the used tanning agent.

[0003] Today the most used process is based on chromium (III) salts (e.g., sulphate or basic sulphate, chloride). That process produces the intermediate product to be then finished, usually called "wet blue". Less used today are processes based on salts of other metals like iron (III), zirconium (IV), titanium (IV), aluminium (III) or a combination of thereof. Those processes produce the intermediate product called "wet white" because of the lighter colour with respect the pale blue of the hide tanned with chromium salts. Other processes do not use metals. There the tanning agent is an organic molecule. The most adopted are tannin (of synthetic or vegetal origin) or different aldehydes (e.g. glutaraldehyde).

[0004] General references about the tanning chemistry can be found in A.F. Holleman, E. Wiberg, "Inorganic Chemistry", Academic Press, (2001); K.H Gustavson, "The Chemistry of Tanning Processes", Academic Press, (1956); A. Covington, Modern Tanning Chemistry, Chem. Soc. Rev., (1997) vol. 26, pp. 111-126.

[0005] Concisely, all the tanning agents reacts with the carboxyl moiety of collagen through a reaction called "olation reaction". Olation is the process by which metal ions form polymeric oxides in aqueous solution and the resulting polymeric clusters are active in cross-linking of the collagen subunits.

[0006] In practice, all the tanning process include three main steps:

(a) a pickling step where the pH of the hide is reduced to low values, generally below 3. This step is necessary because the hides entering the process have been previously treated in alkaline media and the acid conditions are necessary to favor the diffusion of the tanning agent inside the collagen constituting the hide. The pickling step is usually performed by soaking the hide in acid solutions, optionally containing salts able to dissociate and to react with water generating acid conditions.

(b) the proper tanning process where the hide is immersed in an acid solution containing the tanning agent. The step produces a hide containing about 3-5% of metal tanning agent on dry basis, being that content necessary to obtaining a final leather with the desired mechanical properties. Because the diffusion of the olation agent is slow, often other molecules are added to the recipe to speed up the process. In most recipes the addition of these agents induce successive environmental problem during the wastewater treatment. It is very important to maintain significantly acid conditions during this tanning step to avoid the olation reaction that practically stops the diffusion process.

(c) the basification step where the pH of the hide is raised above a critical level in order to promote the olation reaction and consequently stabilize the cross-linking among the collagen and the olation agent. This step is performed by adding basic salts able to neutralize the residual free acidity.

[0007] Overall, the duration of the entire procedure approaches the duration of a day. Several dozens of hides are loaded into a rotating drum, usually heated through steam, and placed in contact with the above described three different solutions. Because of the thermodynamic limitations in the diffusion of the chemicals throughout the hide, a large amount of the used chemicals remains in the exhaust baths. Consequently, successive post treatment processes are necessary for their partial recovery.

[0008] The need is felt of a tanning process overcoming the afore stated technical problems.

SUMMARY OF THE INVENTION

[0009] The applicant has found that it is possible to overcome the above and further technical problem with the process according to the present invention, comprising the following steps.

- a) a pickling step comprising immersing the hides in a bath with an acid and a salt, wherein the pH of the hide is reduced to values lower than 3
 b) tanning step comprising immersing the hide in a bath containing the olating agent,
 c) a basification step comprising immersing the hide in a bath with a basic pH,

wherein in step b) an electric field is produced, by placing the hide between the two electrically powered electrodes.

[0010] The process according to the present invention results to be very versatile as it can be used not only with h the chromium salts, but also with other salts like for example the zirconium, titanium, aluminium salts and also with organic olating agents like, for example vegetal or synthetic tannin, or glutaraldehydes.

[0011] In addition with the process of the invention process time is considerably reduced as well as the volume of the bath in which the hide is dipped.

DESCRIPTION OF THE FIGURES

[0012]

Fig-1A discloses the behavior during electrolysis in water bath of metal ions of a metal salt dissolved in said water bath. This metal salt can be used as olating agent in step b) of the process according to the present invention involving electrolysis. These metal ions, like the hydrogen ions are positively charged in the process conditions of step b) their natural diffusion sustained by the electric field has the direction from the anode to the cathode.

Figure 1B discloses the diagram of the concentration of the hydrogen ions in the cell. They are produced at the anode by the water electrolysis. Then they diffuse forward to the cathode where they are reduced to H₂. Thus the concentration of the hydrogen ions has is maximum value at the anode and its minimum one at the cathode. Accordingly, in terms of pH, the minimum value (i.e. the greater acidity) is at the anode and the maximum one is at the cathode (i.e. where the solution approaches the neutrality)..

Figure 2 represents the application of the mechanism reported in Figure 1, in step b) of the process according to the present invention, wherein 1 indicates Meⁿ⁺ diffusive flux, 2 indicates Meⁿ⁺ electrolytic migration flux, 3 indicates H⁺ electrolytic migration flux, 4 indicates A^{m-} electrolytic migration flux.

Figure 3 represents during electrolysis in water bath the behavior of metal ions of a metal salt used as olating agent dissolved in said water bath in the presence of an anionic membrane.

Figure 4 represents the application of the behavior of the metal ion of a metal salt used as olating agent during electrolysis in the presence of an anionic membrane, if the hide is placed in the anodic compartment during the pickling step (a), the H⁺ ions generated at the anode can be used to neutralize the initial basicity of the hide and to induce its transformation in an acid hide. Figure 4 shows that the use of an anionic membrane has a positive effect also during the tanning step (b) because the positively charged olating agent is kept in the same anodic compartment containing the hide to be tanned and these ions do not migrate in the cathodic compartment of the cell.

Figure 5 represents the application of the behavior of the metal ion and hydrogen ion in the presence of an anionic membrane, when the hide is placed in the cathodic compartment during the basification step (c), H⁺ ions are consumed leading to a pH increase of the hide above the critical value necessary for the olation reaction.

DETAILED DESCRIPTION OF THE INVENTION

[0013] For the purposes of the present invention the definition "comprising" before component(s)/step(s) etc. does not exclude the presence of further element(s)/ step(s), besides those expressly listed, in contrast with the definition "consisting of" after element(s)/step(s) excluding the presence of further elements/ steps besides those expressly mentioned.

[0014] It is well known from the theory of mass transport for electrolytes (see for general references J.M. Bockris, A.K.N. Reddy, "Modern Electrochemistry", Kluwer, (2004)) that the ion flux of an electrolytic specie can be expressed as:

$$\text{Eq. (1)} \quad N_i = uC_i - D_i \nabla C_i - \mu_i z_i C_i F \Delta V$$

where u is the fluid velocity, ∇V is the gradient of electric potential, F is the Faraday constant and C_i , D_i , z_i and μ_i are the concentration, the diffusivity, the electric charge and electric mobility of the ion, respectively. In a stirred system, it

can be assumed that the significant mass transport resistances are located within the hide, being the concentration in the external solution substantially uniform over the spacing L . Being the electrical mobility of ions expressed as $\mu_i = D_i/RT$ and assuming a linear potential gradient, Eq. (1) reduces to:

$$\text{Eq. (2)} \quad N_i = -D_i \nabla C_i - \frac{D_i z_i}{RT} C_i F \frac{\Delta V}{L}$$

[0015] It appears clearly by the exam of equation (2) that the penetration of the ions into the hide can be significantly enhanced by the application of the electric field. Without being bound by any theory it is believed that the electrolytic migration could be the mechanism quantitatively responsible for the penetration of the ions inside the hide.

[0016] In view of the foregoing, it may be advantageous to apply an electric field not only in step b) but also in at least one of the steps a) and c) of the process of the invention.

[0017] According to an aspect of the present invention the process of the invention encompasses that also in the step a), c) or both an electric field is produced, by placing the hide between the two electrically powered electrodes.

[0018] When used in the pickling step a) this electric field increases the diffusions flux of the active ions throughout the hide and in the specific the difference of potential between the two electrodes can exceed that necessary for the water split in hydrogen and oxygen thereby leading to the formation of positive hydrogen ions at the anode. These ions can be then used to generate the acid conditions directly inside the bath during the pickling step.

[0019] For the same reason, positive hydrogen ions can be reduced at the cathode. Accordingly, the consumption of these hydrogen ions leads to a natural pH increase and then this phenomenon can be used in the basification step.

[0020] As previously reported the figures 1 and 3 report the mechanism of action of water electrolysis carried out in a water bath containing ion metals respectively without and in the presence of anionic membranes. Whereas Figures 2, 4 and 5 represent preferred embodiments of the process of the invention involving the application of the electrolysis concepts in Figure 1 and 3.

[0021] As illustrated in Figure 1A being the metal ions adopted for the tanning positively charged in the process conditions, their natural diffusion sustained by the electric field has the direction from the anode to the cathode Figure 1B discloses the diagram of the concentration of the hydrogen ions in the cell. They are produced at the anode by the water electrolysis. Then they diffuse forward to the cathode where they are reduced to H₂. Thus the concentration of the hydrogen ions has is maximum value at the anode and its minimum one at the cathode. Accordingly, in terms of pH, the minimum value (i.e. the greater acidity) is at the anode and the maximum one is at the cathode (i.e. where the solution approaches the neutrality).

[0022] As illustrated in Figure 2, this phenomenon can be used to speed up the tanning step (b) even two-fold or more with respect the pure diffusive conditions. The enhancement factor is controlled by the applied electric potential difference between the two electrodes. Being the process time determined by the full and uniform penetration of the olation agent through the hide, obviously doubling the penetration speed the process time halves.

[0023] It is naturally to think that process can be applied when the tanning is obtained through metal ions like chrome (III), iron (III), aluminum (III), titanium (VI) and zirconium (VI). However, when considering that in acid media also most of the organic molecules adopted for this scope, like tannin, are hydrolyzed, it is clear that the electrochemical enhancement can be adopted also in these cases.

[0024] As in all the electrochemistry processes, also in the process according to the present invention a membrane can be introduced in between the two electrodes to create an anodic and a cathodic compartment. With reference to Figure 3. if the selected membrane is an anionic membrane, that is a membrane that inhibits the permeation of positive ions while admits the migration of the negative ones, the following effects can be produced during the process:

- a decrease of the pH value in the anodic compartment;
- an increase of the pH value in the cathodic compartment.

[0025] Accordingly, as illustrated in Figure 4, if the hide is placed in the anodic compartment during the pickling step (a), the H⁺ ions generated at the anode can be used to neutralize the initial basicity of the hide and to induce its transformation in an acid hide.

[0026] On the contrary, as illustrated in Figure 5, placing the hide in the cathodic compartment during the basification step (c), H⁺ ions are consumed leading to a pH increase of the hide above the critical value necessary for the olation reaction.

[0027] Figure 4 shows that the use of an anionic membrane has a positive effect also during the tanning step (b) because the positively charged olating agent is kept in the same anodic compartment containing the hide to be tanned and these ions do not migrate in the cathodic compartment of the cell.

[0028] The difference of potential to be applied to the two electrodes is a function of the distance between them and of the thickness of the hide to be tanned. Accordingly, it is of interest to reduce the energy consumption, to reduce the space between the electrodes. This produces the positive effect to significantly reduce the volume of the bath. Thus, this electrochemically enhanced tanning process has the advantage of using very small solution / hide volume ratio.

[0029] Moreover, because the diffusion of the tanning agent into the hide is only slightly dependent from the concentration gradient, the applied electric potential can be adopted to produce a very high utilization of the chemicals of the bath. The electric potential can be also adjusted throughout the process, being the potential increase able to compensate the concentration reduction in the bath to keep almost constant the mass flux.

[0030] The following examples are reported for illustrative but not limitative purposes.

Example no. 1. Electrochemical enhancement of the tanning step using chrome (III) salts

[0031] A hide of about 25 cm² area, already acidified by a pickling step is placed in an electrochemical cell filled with a solution of 10% CrSO₄ at pH=2 and a temperature up to 60°C. A difference of potential of 10 V is applied to the electrodes. After 20 min the hide is extracted and rinsed. The chemical analysis revealed a uniform concentration of 2% Cr through all the thickness. The same experiment is repeated without applying the potential differences to the electrodes; at the same time the hide appears not uniformly penetrated by Cr ions evidencing a significant part of its section not still reached by Cr.

Example no. 2. Electrochemical enhancement of the tanning step using other chrome (III) salts

[0032] A hide of about 11.5 cm² area, already acidified by pickling step is placed in an electrochemical cell filled with a solution of 13% CrCl₃ and 3% of complexing agent at pH = 2 and a temperature of 25 °C. A difference of potential is applied to the electrodes and after 30 min the hide is extracted and rinsed. The same experiment is repeated without applying the potential difference to the electrodes. Chemical analyses revealed that the concentration of chromium is about 2 times higher in the process with the application of the voltage: hence, the process is two times faster than the normal conditions. The application of the potential differences is related to a uniform concentration through the whole thickness, while in the other case without current the hide appears not uniformly penetrated by Cr ions.

Example no. 3. Electrochemical enhancement of the pickling step

[0033] A hide of about 25 cm² area, is placed in the anodic compartment of an electrochemical cell created by an anionic membrane placed in between the two electrodes. The cell is filled with a solution H₂SO₄ at pH=2 and a temperature up to 60°C. A difference of potential of 10 V is applied to the electrodes. After 20 min the hide is extracted and rinsed. Then the leather is analyzed by titration evidencing its full acidification.

Example no. 4. Electrochemical enhancement of the basification step

[0034] A hide of about 20 cm² area, already pickled and tanned according to procedure described in Example 2, has been soaked in the cathodic compartment of Figure 5. A difference potential of 30 V has been applied to the electrodes, where the cathode is made of platinized titanium mesh. The initial acidic pH of the cathodic compartment solution raises from pH ~ 2 to pH ~ 4.5 in 2 hours, avoiding the use of alkalinizing agents for the basification step.

Example no. 5. Electrochemical enhancement of the tanning step using Titanium (IV) salts

[0035] A hide of about 11.5 cm² area, already acidified by a pickling step, is placed in an electrochemical cell filled with a solution of 1% titanyl sulphate at a pH = 2 and a temperature of 25 °C. A difference of potential is applied to the electrodes and after 30 min the hide is extracted and rinsed. The same experiment is repeated without applying the potential difference to the electrodes. Chemical analyses revealed a uniform concentration of 1.5% titanium on the whole thickness for the process with the application of the voltage, while in the other case (without current) a non-uniform penetration of titanium ions is detected.

Example no. 6. Electrochemical enhancement of the tanning step using tannin

[0036] A hide of about 11.5 cm² area, already acidified by a pickling step, is placed in an electrochemical cell filled with a solution of 18% tara tannins at a pH = 2 and a temperature of 25 °C. A difference of potential is applied to the electrodes and after 120 min the hide is extracted and rinsed. The same experiment is repeated without applying the potential difference to the electrodes. Chemical analyses revealed a uniform concentration of 1% tannin on the whole

thickness for the process with the application of the voltage, while in the other case (without current) a non-uniform penetration of tannin ions is detected.

Example no. 7. Electrochemical enhancement of the tanning step using iron (II) salts

[0037] A hide of about 11.5 cm² area, already acidified by pickling step, is placed in an electrochemical cell with a solution of 25% iron sulphate and 12% of complexing agent at a pH = 2 and a temperature of 25°C, Figure 6. A potential difference is applied to the electrodes and after 30 min the hide is extracted and rinsed. The same experiment is repeated without applying the potential difference to the electrodes. Chemical analyses revealed that the concentration of iron through all the thickness is uniform and about 2 times higher than the case without the application of the potential (here the iron ions distribution is not uniform and not the whole thickness is reached by them). Hence, the application of the voltage is twice more efficient than the process without the potential difference.

Claims

1. A process for tanning hide comprising the following steps:

- a) a pickling step comprising immersing the hides in a bath with an acid and a salt, wherein the pH of the hide is reduced to values lower than 3
- b) tanning step comprising immersing the hide in a bath containing the tanning agent,
- c) a basification step comprising immersing the hide in a bath with a basic pH,

wherein in step b) an electric field is produced, by placing the hide between the two electrically powered electrodes.

2. The process according to claim 1, wherein also in the step a), c) or both an electric field is produced, by placing the hide between two electrically powered electrodes.

3. The process according to any one of claims 1-2, wherein an anionic membrane separates the anionic compartment from the cathodic compartment and the hide is placed in the anodic compartment.

4. The process according to claim 3, wherein also in step a) an electric field is produced, by placing the hide between the two electrically powered electrodes.

5. The process according to anyone of claims 1 or 2 wherein an anionic membrane separates the anionic from the cathodic compartment and the hide is placed in the cathodic compartment.

6. The process according to claim 5, wherein also in step c) an electric field is produced, by placing the hide between the two electrically powered electrodes.

7. The process according to anyone of claims 1-6, wherein the tanning agent is selected from chromium, zirconium, titanium, aluminium salts or organic tanning agents.

8. The process according to claim 7, wherein the organic tanning agent is selected from vegetal or synthetic tannin or glutaraldehyde.

Fig.1 A

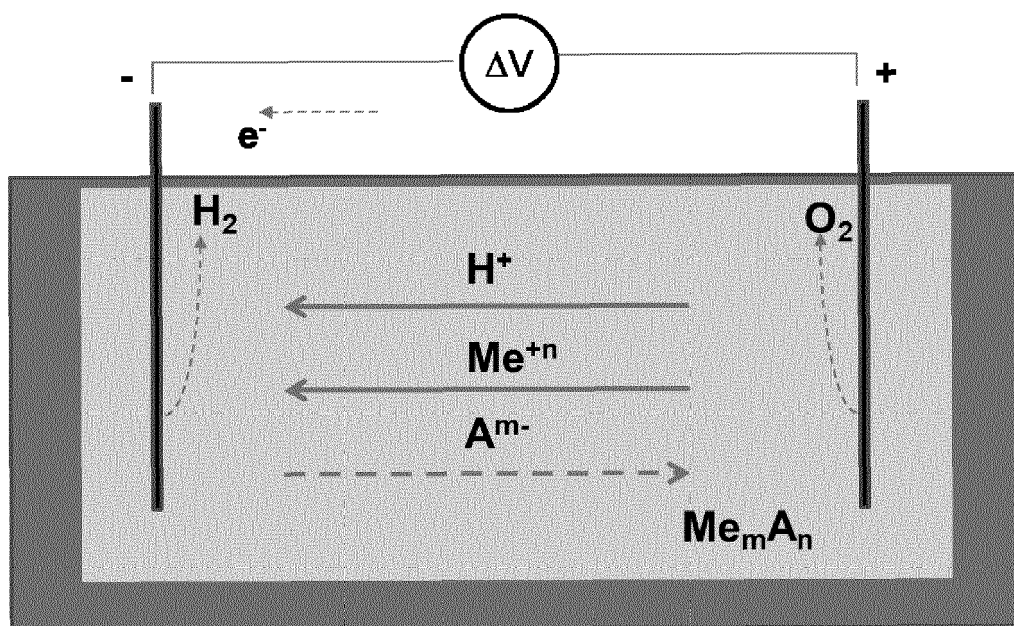


Fig. 1 B

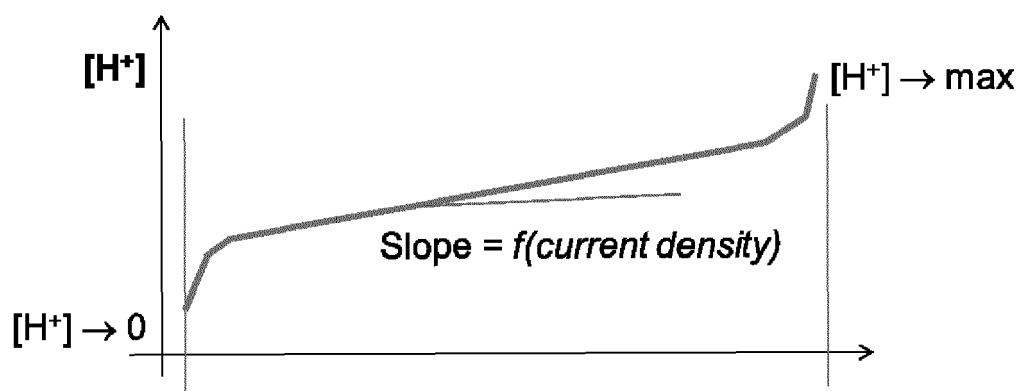


Fig.2

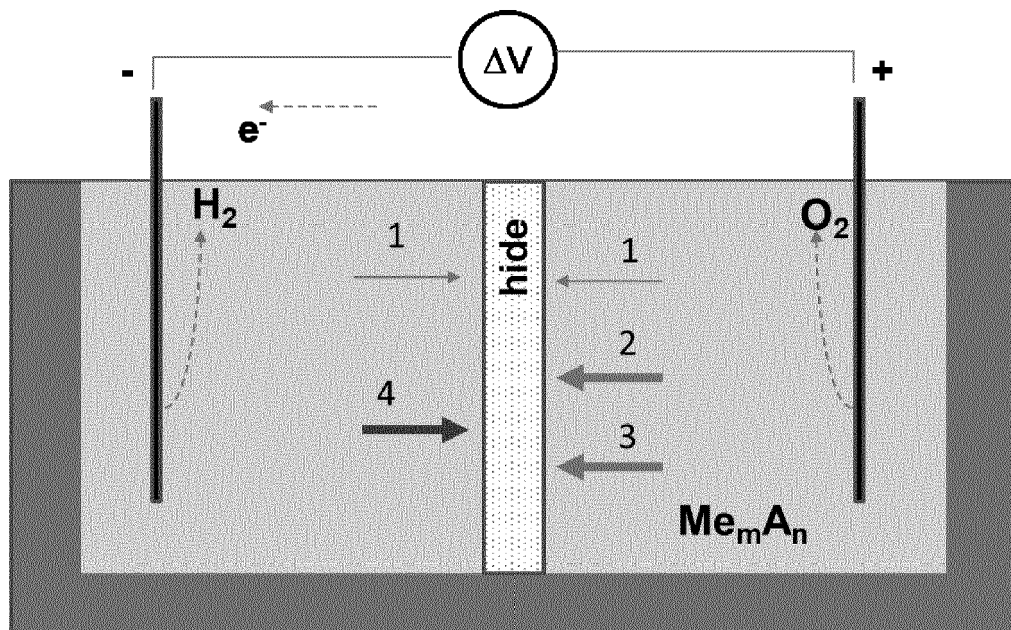


Fig.3

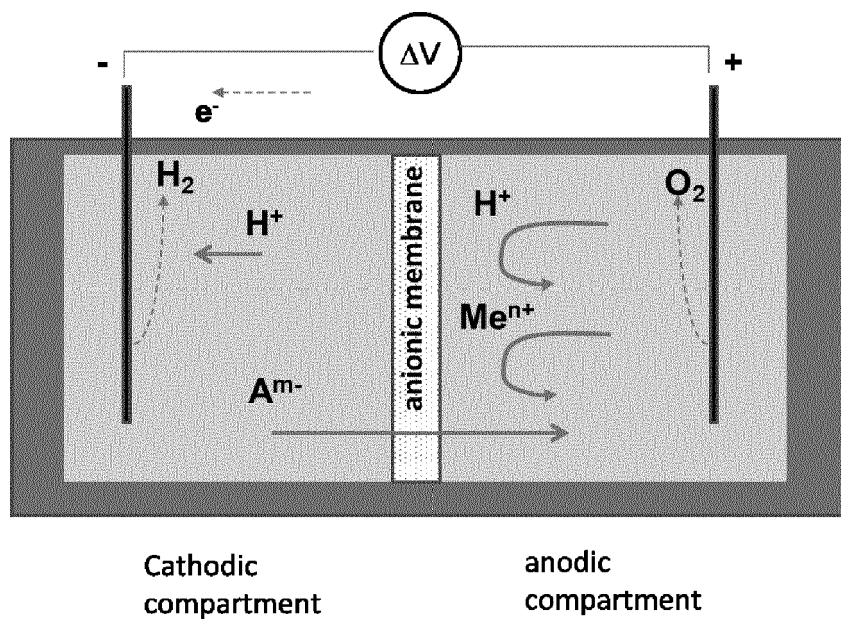


Fig.4

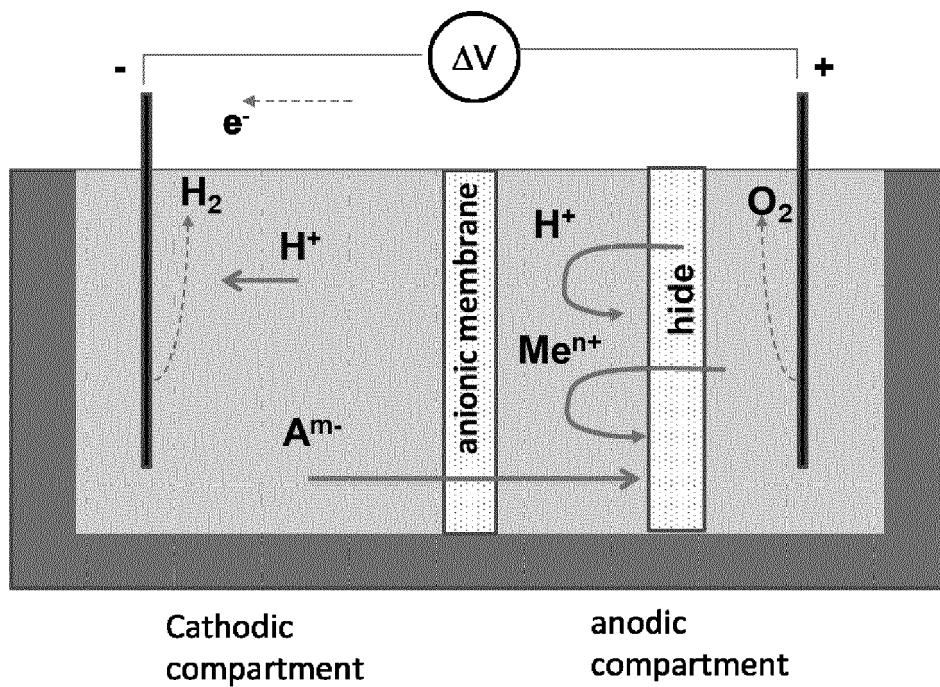
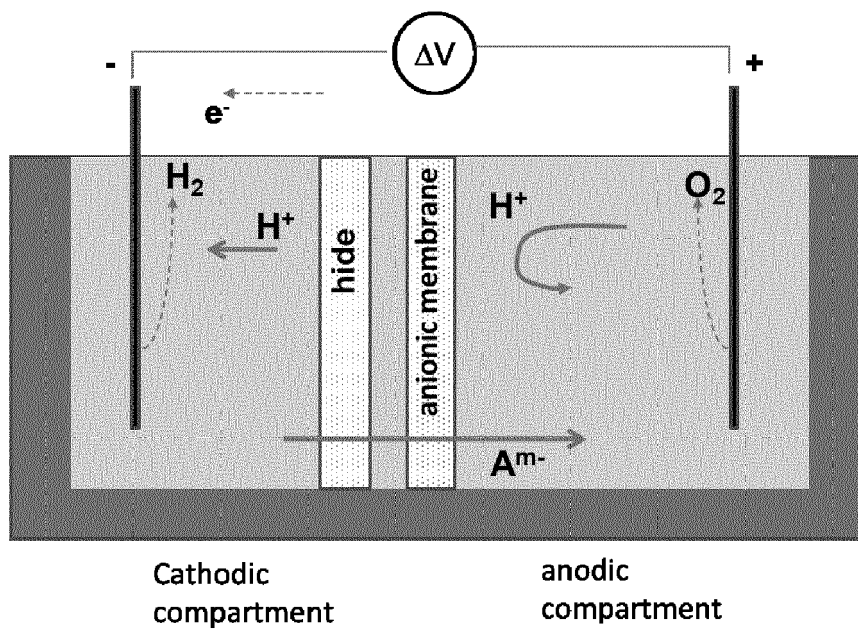


Fig. 5





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 Application Number
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X	DATABASE WPI Week 199141 Thomson Scientific, London, GB; AN 1991-301567 XP002785810, & SU 1 624 026 A (KURSK LEATHER FOOTW) 30 January 1991 (1991-01-30) * abstract *	1-7	INV. C14C3/04 C14C3/06 C14C3/10 C14C3/16 C14C3/30 C14C15/00
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Place of search Munich		Date of completion of the search 12 June 2019	Examiner Neugebauer, Ute
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 19 15 6703

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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