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(54) **A PROCESS FOR THE MANUFACTURE OF A BIO-BASED AND VEGAN FAUX LEATHER MATERIAL**

(57) The present invention refers to a process with reduced environmental impact for the production of a bio-based imitation leather material by treating a polyurethane coagulate, which allows to obtain a vegan material, printable to achieve the same appearance as natural leather. This material has also greatly improved

physical and mechanics characteristics that make it useful for the most varied applications, in the fashion sector, in particular to create and / or decorate clothing, footwear and leather goods, in the furniture and design sector, and in any other related sector.

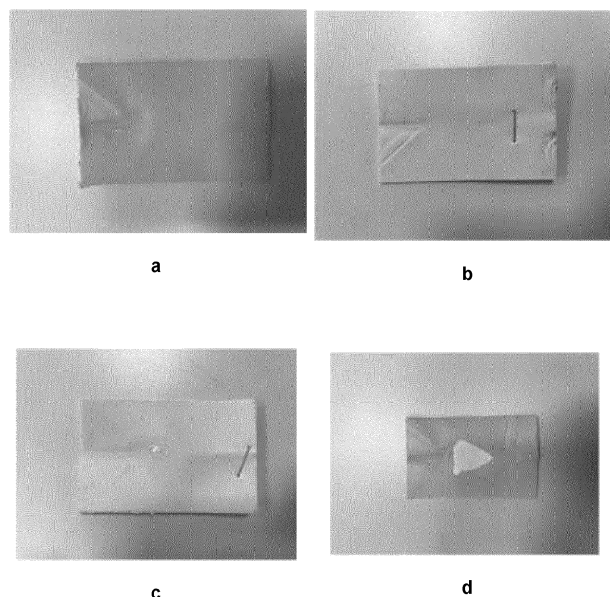


Fig. 1

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Description

Field of the Invention

[0001] The present invention generally relates to the field of the treatment of materials, and more precisely, it refers to a process with reduced environmental impact for the production of a bio-based and vegan imitation leather material, i.e. a material derived completely or at least partially from renewable sources and free of materials of animal origin. The invention also relates to the material obtainable with this process, which is printable to provide the appearance of natural leather and characterized by improved mechanical strength and durability, useful for ensuring high quality performance in a wide range of applications.

State of the Art

[0002] In recent years, consumer demand for products of non-animal origin has increased not only in the food sector, but also in other sectors, including clothing, fashion accessories and footwear. These products, free from materials of animal origin, are commonly classified as *vegan*. In addition to these requests, there is often also the request for products with a reduced environmental impact and the use of materials from renewable sources, which reduce the use of synthetic materials of fossil origin. Materials of this type, which are completely or at least partially derived from renewable sources, are commonly referred to as *bio-based* materials.

[0003] However, products made with these materials are always required to have a pleasant aesthetic appearance, as similar as possible to the appearance of animal hides, which the consumer is obviously not willing to give up, and increasingly higher quality performance, as well as more or less high workability and resistance depending on the application and intended use.

[0004] In particular, in the case of synthetic leathers intended for the production of bags, shoes or other accessories, the physical and mechanical characteristics required from the material are particularly stringent. As a matter of fact, the material must guarantee sufficient strength and resistance to be able to be sewn, for example, or in any case joined to portions of the same or a different material, to make the finished product in the form of a bag, shoe, belt, and the like.

[0005] In order to aspire to obtain a material with these characteristics, the bio-based raw materials must obviously be selected with appropriate sustainability characteristics and be subjected to specific, suitable treatments. In their turn, these treatments must guarantee the desired ecology not only of the final product following the treatment, but also of the process itself and of the reagents and solvents used to carry it out.

[0006] The environmental sustainability of industrial production is a new fundamental request to be aligned with for all kinds of production, with a view to oppose

against the environmental degradation and the destruction of natural ecosystems, as well as to respect even the most stringent environmental regulations and to guarantee the health of workers in all stages of the production chain.

[0007] To date, several attempts have been made to meet the market demands illustrated above, but as far as the Applicant is aware, none of these are completely satisfactory, i.e. it is configured as a material not of animal origin but with the appearance of animal hide, with reduced environmental impact and with good strength and mechanical resistance.

[0008] The need is therefore still felt to have available an ecological treatment process, with a reduced environmental impact, of sustainable raw materials, capable of providing a high quality vegan material, endowed with the durability and resistance necessary to make it suitable for use in the clothing, accessories and footwear sector, also having the softness to the touch and the aesthetic appearance of animal leather.

Summary of the Invention

[0009] Now the Applicant has found a process for the manufacture of a faux leather material with reduced environmental impact described below. This process, by treating a bio-based polyurethane coagulate obtained from renewable sources and with reduced environmental impact, allows obtaining a durable a mechanically resistant material, completely analogous to a natural leather both in terms of softness to the touch and in terms of surface appearance once printed.

[0010] Advantageously, the production process of this invention provides for a limited use of chemicals and water, in significantly lower amount than that found in the treatment of animal hides. In particular, the process of this invention is free from chromium or other metal treatments, and all chemicals used are compliant with MRSL (*Manufacturing Restricted Substance List*) ZDHC (*Zero Discharge of Hazardous Chemicals*) that limits the use of hazardous chemicals in manufacture processes.

[0011] It is therefore a subject of present invention a process for the manufacture of a bio-based faux leather material, as defined in the first of the claims annexed herein.

[0012] A bio-based faux leather material obtainable by this process, its use as replacement material for the animal leather and an article made with it, as respectively defined in the related independent claims annexed herein.

[0013] Further important characteristics of the process for manufacturing a bio-based faux leather material, of the so obtained material and of its use, as well as of the articles made with the material according to the invention are disclosed in the following detailed description.

Brief Description of the Drawings

[0014]

Figure 1a shows an intact sample of the material of the present invention after mechanical strength dry test described in the following Example 1.

Figure 1b shows an intact sample of the material of the present invention after mechanical strength dry test described in the following Example 1.

Figure 1c (comparison) shows a degraded sample of a material not treated by the process of the present invention after mechanical strength dry test described in the following Example 2.

Figure 1d (comparison) shows a degraded sample of a material not treated by the process of the present invention after mechanical strength wet test described in the following Example 2.

Detailed Description of the Invention

[0015] In the following description, if not otherwise specified, the percentage amounts are expressed as weight percentages with respect to total weight of the composition comprising them.

[0016] The Applicant has found that by treating a bio-based polyurethane coagulate with synthetic tannins in water and applying a polyurethane adhesive to the surface thus treated, the coagulate acquires characteristics of high mechanical resistance, improved with respect to the starting product, and a much greater stability and durability over time, also providing a soft and flexible surface which, following printing, is completely analogous to that of natural leather.

[0017] In the present invention, the term "*bio-based*" means "completely or at least partially derived from renewable sources".

[0018] Moreover, by the expression "*bio-based* polyurethane coagulate" is meant herein a product obtained by coagulation of polyurethane obtained from renewable sources on a fabric or on non-woven fabric support. Various methods for the preparation of such materials have been known for decades; in this invention preferred starting materials are polyurethane coagulates prepared by direct coating of the support with polyurethane in water. The support of the present polyurethane coagulate can be made, for example, with a fabric made of natural and / or artificial fibres on which polyurethane has been applied by coagulation. Preferably, these natural and / or artificial fibres are selected from linen, cotton, hemp, viscose, and blends thereof. Among these, viscose is preferred, classifiable as an artificial fibre since it is of natural origin from cellulose, but obtained by chemical and mechanical processing of the cellulose. According to the FSC (Forest Stewardship Council) certification system, cellulose comes from responsibly managed forests.

[0019] The term "*vegan*" as used herein means "free from materials of animal origin".

[0020] In an aspect of the process of this invention, the polyurethane coagulate is a bio-based polyurethane coagulate on a viscose fabric, consisting essentially of polyurethane obtained from renewable sources and viscose, for instance consisting of approximately 30% of viscose and approximately 70% of polyurethane.

[0021] By the term "synthetic tannins" is meant in this invention tannic acid derivatives of synthetic origin that are substitution tannins with a reduced environmental impact, selected for example from phenolic, arylsulphonic, hydroxyarylsulphonic, dihydroxydiphenylsulfonic derivatives, and their mixtures or condensation products thereof. According to this invention, the term "synthetic tannins" preferably refers to arylsulphonic and hydroxyarylsulphonic derivatives, and more preferably, it refers to condensation products by a methylene bond between arylsulphonic and hydroxyarylsulphonic acids.

[0022] The process for the manufacture of a faux leather material from renewable sources and not of animal origin of this invention, free from treatments with chrome and other metals and having reduced environmental impact, comprises the steps of:

- i) wetting with water a polyurethane coagulate from renewable sources in a drum;
- ii) treating said coagulate with synthetic tannins by their addition into said drum;
- iii) drying and applying by spraying and/or rolling a polyurethane adhesive agent.

[0023] The wetting of the coagulate with water in step i) of this process is carried out for the time necessary to completely and uniformly wet the coagulate tissue, for example for a time of about 30 minutes. In an aspect of this invention, the amount of water used is about 200 litres per 10 meters of treated coagulate having a width of about 1.5 meters, a much lower quantity than that usually used in tanning treatments. Furthermore, the temperature in this step is preferably the room temperature and no other additives are added to water, such as surfactants, in order to create a process with a reduced environmental impact in all its aspects and in the various steps.

[0024] Advantageously, in the present process, step ii) of treatment with synthetic tannins can be carried out without draining the water from the drum, but simply adding the powdered tannins into the drum at the end of the wetting. For example these tannins are added in an amount equal to about 6 % by weight with respect to the dry weight of the coagulate to be treated, and leaving the material in the bath for about 30 minutes. In an aspect of the process, the pH of this step ii) is brought to a pH of between 5 and 6, preferably to a pH of approximately 5.2.

[0025] If a material with a particular colour is desired, after the treatment with tannins, the present process can optionally comprise a dyeing phase which can be advantageously carried out in the same drum, without discharg-

ing the aqueous solution coming from step ii), by adding one or more dyeing agents, preferably selected from azo dyes. Optimal results in terms of durability and fastness of colours on the material of the invention have in fact been observed using this type of dyes in combination with the treatment with the synthetic tannins described above.

[0026] In a particular embodiment of the process of the invention, after the treatment with tannins in step ii), or after the dyeing step if present, before extracting the treated material from the drum and drying it, one or more fixing operations are carried out by addition of a fixative agent, typically formic acid. This treatment causes a lowering of the pH, which assists the fixing of the treatment products inside the material.

[0027] In step iii) of this process, the drying of the material can be carried out with any drying method suitable for the purpose, in the conditions that any person skilled in this field could identify on the sole basis of their ordinary knowledge. In a preferred aspect of the present process, the panels of the material discharged from the drum after the step of treatment with tannins or after the colouring step, if present, are dried at room temperature by winding in the appropriate machinery. In this way, about 90% of the water is removed from the material, without heating, as is usually the case for drying these materials.

[0028] Optionally, to quickly and completely remove the last part of the remaining water, in this step the panels of the material can be subjected to forced drying, for example at a temperature of about 45°C. An effective forced drying method can for example be achieved as in the traditional drying of animal hides by means of a catenary, i.e. placing the material to be dried suspended in air, hanged on special chains to allow it to disperse the last residual moisture present inside the material.

[0029] Once dried, in step iii) of the present process a polyurethane adhesive agent is applied onto the material by spray application or, preferably, by means of a roller, until a uniform layer is formed on the material. In a preferred embodiment of the present process, the polyurethane adhesive agent is an aliphatic polyurethane adhesive. The agents of this family have in fact been identified by the inventors as the best performing products to achieve the desired and necessary adhesion of the finishing layers that will be subsequently applied.

[0030] In a particular embodiment, before and/or after the application of the polyurethane adhesive agent, the present process provides for the application on the dry material, by spray and/or roller, of an anti-dusting agent, selected for example among the water-based acrylic/polyurethanic agents commonly used in the finishing processes of the tanning industry.

[0031] In an embodiment of the invention, the present process may also comprise one or more finishing steps by using chemical or mechanical means, to obtain the desired visual or tactile effect; and/or a step of printing the material according to a desired pattern, for example by means of engraving plates or printing machines for

leather. Both the one or more finishing steps and the printing step can be carried out according to the methods and with the machinery and reagents commonly used in the treatment of animal hides. The inventors have been able to verify that these finishing and/or printing steps carried out on the material of the invention, first treated with tannins and with the polyurethane adhesive, result in a particularly attractive finished product similar to the appearance and touch of animal hides.

[0032] Most of the steps of the process of this invention can be advantageously carried out at room temperature, for example around 20°C, without any expenditures of energy for heating, thus also contributing in this way to environmental sustainability. Furthermore, the only solvent used in the process of the invention in significant quantities, although lower than the quantities used in known processes, is water, and the pH, contrary to known processes, is kept at values not too far from neutral pH.

[0033] The bio-based imitation leather material obtained with the process described above, which is also subject of this invention, can be used as a replacement for animal hides in any sector, to decorate or make clothing and accessories items, including bags and footwear, but also to cover design objects and furniture, or the interior of cars.

[0034] The advantages linked to the present invention are manifold. First, the material resulting from the production process of this invention is particularly attractive once it is printed and soft to the touch, completely similar to animal leather while not having any animal derivation and therefore being a vegan material.

[0035] As already mentioned above, all steps of the invention process are moreover carried out in conditions of reduced environmental impact, using non-toxic and not harmful reagents and solvents, under environmentally sustainable temperature and energy consumption conditions. In particular, the present process does not use the metal salts, chromium salts in particular, typical of the traditional tanning processes, giving rise to a finished material that can be metal-free and chrome-free.

[0036] Furthermore, the material obtainable with the process of this invention has acquired much better mechanical properties than those of the starting coagulate so much so that with the material of this invention it has been possible to make complex items such as bags and shoes, by sewing parts of material, cut according to patterns. More in general, for polyurethane coagulates, this process has the surprising effect of improving their functional and performance characteristics, giving rise to a highly performing finished material from a physical and mechanical point of view, extremely durable and stable over time, even as regards colours. Thanks to these characteristics, the material thus obtained can be used successfully not only in the fashion sector, in particular to create and/or decorate clothing and leather goods, but also in the furniture and design sector, and in any other related sector.

[0037] A further advantage of the process of this in-

vention lies in its simplicity, cheapness and in the fact that each process step it can be carried out using pre-existing machinery and systems used up to now for the tanning treatments of animal hides.

[0038] The invention is described in the following by means of examples without however being limited thereto: it is understood that the quantities and percentages of the reagents described can be varied, as well as the type of reactors and more in general the conditions used while remaining in the same scope of the present invention.

Example 1

[0039] In a tanning drum, panels measuring 100 cm x 145 cm of polyurethane and viscose coagulate were inserted and kept for about 30 minutes in a water bath at 20°C, added to the drum in the measure of 200 litres every 10 panels of material.

[0040] Without discharging water and always at a temperature of 20°C, powdered synthetic tannins were added to the drum, i.e. condensation product with a methylene bond of arylsulphonic and hydroxyarylsulphonic acids in a measure of 16% by weight on the weight of the starting coagulate panels to be treated. The material was kept in this treatment bath for approximately 30 minutes at a pH of the solution of approximately 5.2. An azo dye in an amount of 20% by weight was then added and the material was kept in this dyeing bath for about 30 minutes.

[0041] At the end of the dyeing, formic acid was added in three portions for fixing the previous treatments, in a first phase of 4 hours 12% of formic acid was added, in a second phase of 30 minutes 4% of formic acid and in a third step of a further 30 minutes 4% formic acid.

[0042] The material thus treated was extracted from the drum and dried at room temperature by winding in a special machine generally used in leather tanning, then the panels obtained from this first drying were hanged in the catenary and subjected to forced drying at 45°C.

[0043] A layer of aliphatic polyurethane adhesive in solvent was rolled onto the dry material, which allows the treated base to melt in subsequent finishing applications. Multiple finishing coating layers of water-based acrylic polyurethane were then applied with a roller and spray machine, before passing the material to print a pattern on a hot plate press.

[0044] The material thus obtained appeared soft to the touch, with an appearance completely similar to that of a leather tanned from animal leather. Furthermore, this material showed better mechanical resistance performances, evaluated by the inventors in particular as resistance to bending in the following experimental tests.

[0045] A sample of the material of the invention treated as described above was subjected to a flexural strength test by using a "Bally" flexometer according to the standard procedures described in the UNI EN ISO 5402-1: 2017 Standard with the following results. After 100,000 flexures under dry conditions, the sample of the present

material showed no sign of breakage (test result: PASS; Figure 1a). Equally, no sign of breakage was highlighted after 30,000 flexures under wet conditions (test result: PASS; Figure 2b).

Example 2 (COMPARISON)

[0046] The same starting polyurethane and viscose coagulate of Example 1 above, not treated with the process of the invention, was subjected to the same mechanical resistance tests described above, in particular to bending resistance tests using a "Bally" flexometer according to the same procedures standard of the aforementioned standard mentioned above.

[0047] Already after 20,000 flexures under dry conditions there was a very serious break in the material (test result: FAIL; Figure 1c), while only 1,000 flexures under wet conditions caused a very serious peeling of the material (test result: FAIL; Figure 1d).

[0048] The material not treated with the process of this invention therefore does not have the necessary mechanical strength for use in a similar way to animal hides, and it does not even possess suitable visual and tactile characteristics, as it can also be seen from the images in the figures.

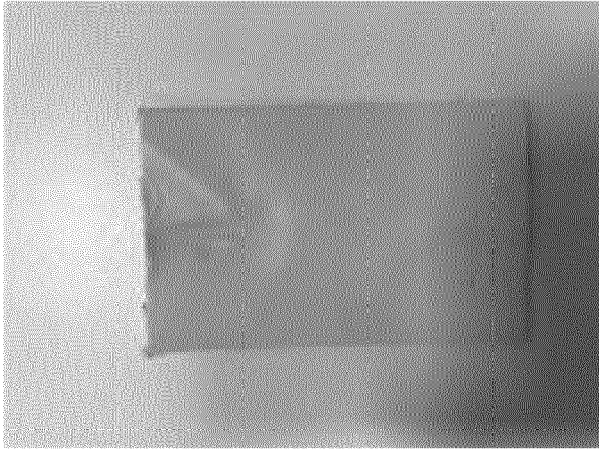
[0049] The present invention has been described up to now with reference to a preferred embodiment. It is to be understood that there may be other embodiments that pertain to the same inventive core, as defined by the scope of the claims set out below.

Claims

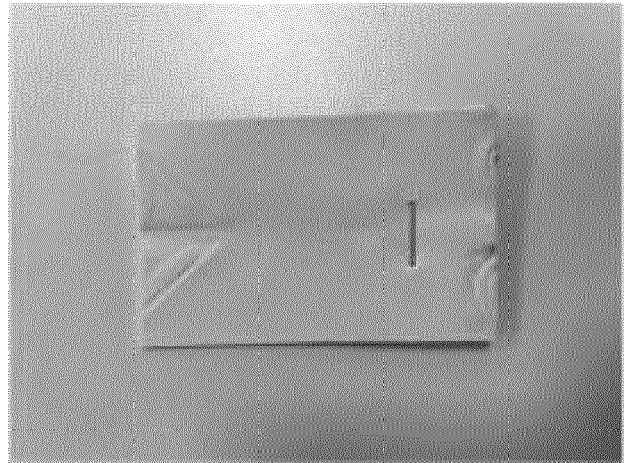
1. A process for the manufacture of a faux leather material, *bio-based* and *vegan*, with reduced environmental impact and free from treatments with metal salts, comprising the steps of:
 - iv) wetting with water a polyurethane coagulate from renewable sources in a drum;
 - v) treating said coagulate with synthetic tannins by their addition into said drum;
 - vi) drying and applying by spraying and/or rolling a polyurethane adhesive agent.
2. The process according to claim 1, further comprising a colouring step with azo dyes between said step ii) of treating with tannins and said step iii) of drying.
3. The process according to any one of the claims 1 or 2, further comprising a step of fixation at acid pH between said step ii) of treating with tannins and said step iii) of drying or, if present, immediately after said colouring step.
4. The process of any one of the preceding claims, wherein said polyurethane coagulate is a fabric in

natural and/or artificial fibres on which polyurethane from renewable sources has been applied by coagulation.

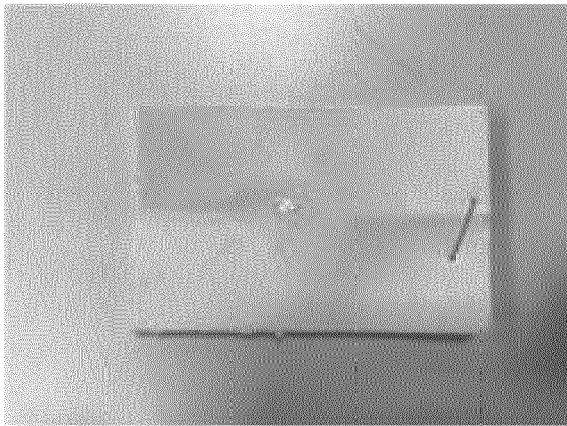
5. The process according to claim 4, wherein said natural and/or artificial fibres are selected from linen, cotton, hemp, viscose, and blends thereof. 5
6. The process of any one of the preceding claims, wherein said polyurethane coagulate essentially consists of viscose and polyurethane from renewable sources. 10
7. The process of any one of the preceding claims, wherein said synthetic tannins are substitution tannins with reduced environmental impact selected from phenolic, aryl sulphonic, hydroxylaryl sulphonic, dihydroxy diphenylsulphonic compounds, mixtures thereof and condensation products thereof. 15
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8. The process according to claim 7, wherein said synthetic tannins are condensation products by methylene bond of aryl sulphonic and hydroxyaryl sulphonic acids. 25
9. The process of any one of the preceding claims, wherein polyurethane adhesive agent is an aliphatic polyurethane adhesive.
10. The process of any one of the preceding claims, further comprising applying an anti-dusting agent, by spraying and/or rolling, on said material following drying and before and/or after application of said polyurethane adhesive agent. 30
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11. The process according to claim 10, wherein said anti-dusting agent is selected from acrylic/polyurethanic agents.
12. The process according to any one of the preceding claims, further comprising finishing and/or printing steps of the material coming from said step iii) of drying and applying an adhesive agent. 40
13. A faux leather material, *bio-based* and *vegan*, obtainable by the process of manufacture of the claims 1-12, said material being a polyurethane coagulate coming from renewable sources treated by said process and having the tactile and visual characteristics of the animal leather and improved durability, colourfastness and mechanical resistance with respect to the starting polyurethane coagulate. 45
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14. Use of a faux leather material as defined in claim 13, as replacement material for animal leather. 55
15. An article made, completely or partially, with the faux leather material as defined in claim 13.



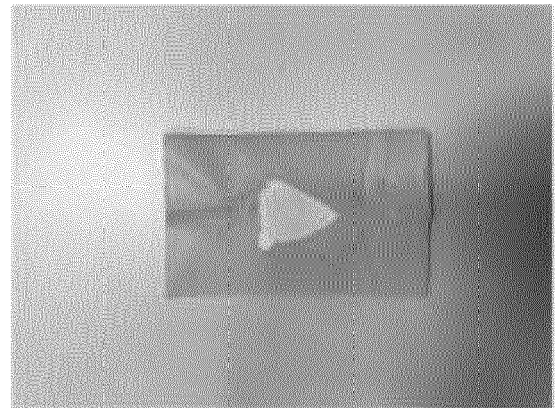
a



b



c



d

Fig. 1



EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	KR 2018 0126735 A (HYUNDAI MOTOR CO LTD [KR]; BAIKSAN CO LTD [KR] ET AL.) 28 November 2018 (2018-11-28) * paragraph [0001] * * paragraph [0051] * * claim 1 *	1-15	INV. D06N3/00 D06N3/14
A	EP 0 165 345 B1 (TORAY INDUSTRIES [JP]) 23 August 1989 (1989-08-23) * page 12, lines 14-32 *	1-15	
			TECHNICAL FIELDS SEARCHED (IPC) D06N
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 30 May 2022	Examiner Queste, Sébastien
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 20180126735 A	28-11-2018	CN 108948313 A	07-12-2018
		KR 20180126735 A	28-11-2018
		US 2018334773 A1	22-11-2018
EP 0165345 B1	23-08-1989	EP 0165345 A1	27-12-1985
		JP S59150133 A	28-08-1984

EPO FORM P0459

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