



(12)

EUROPEAN PATENT APPLICATION

(43)

Date of publication:
02.10.2024 Bulletin 2024/40

(51)

International Patent Classification (IPC):
C14B 1/44 (2006.01) B24C 1/00 (2006.01)

(21)

Application number: 24167883.8

(52)

Cooperative Patent Classification (CPC):
C14B 1/44; B24C 1/003

(22)

Date of filing: 29.03.2024

(84) Designated Contracting States: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR Designated Extension States: BA Designated Validation States: GE KH MA MD TN (30) Priority: 30.03.2023 IT 202300006228 (71) Applicant: Politecnico di Milano 20133 Milano (IT)	(72) Inventors: - Masi, Maurizio 20124 Milano MI (IT) - Rossi, Filippo 52100 Arezzo AR (IT) - Salmi, Omar 20131 Milano MI (IT) (74) Representative: Perani & Partners S.p.A. Piazza Armando Diaz, 7 20123 Milano (IT)
---	--

(54)

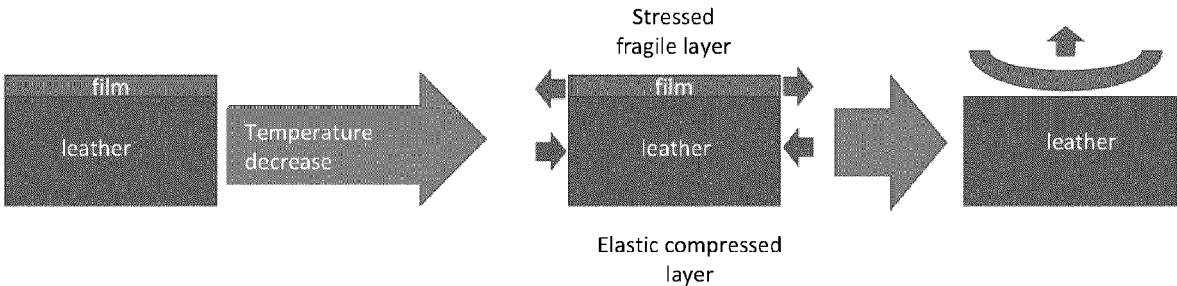
A METHOD FOR REMOVING FINISHING LAYERS FROM TANNED AND FINISHED LEATHER

(57)

A process for removing a finishing layer from finished leather, comprising the following steps:
A. providing a finished leather comprising a surface polymeric layer applied on said leather;
B. subjecting the finished leather to a quick freezing;

C. removing the surface polymeric layer from the finished leather,
wherein
step B is carried out by employing a cryogenic inert material.

Fig. 1



Description**FIELD OF THE INVENTION**

5 **[0001]** The technical field to which the invention pertains is that of methods for removing finishing layers from tanned and finished leathers.

BACKGROUND ART

10 **[0002]** Most leather goods, deriving from tanned animal skins, are subjected to surface finishing treatments which modify the surface appearance of the leather and often impart waterproof properties. Such a characteristic is obtained by depositing a thin polymeric film having a thickness of a few microns.

15 **[0003]** However, not all finished leathers get a commercial placement and, as a result, they accumulate in tannery warehouses until they have to be disposed of in landfills. Indeed, the surface finishing is affected by seasonality and current trends; therefore, the commercial value of the finished leathers may suffer sudden declines.

20 **[0004]** In this regard, techniques for removing the surface layer, such as shaving processes, are known, which result in removing a thickness of even 1 mm and, therefore, do not allow sufficiently thin layers of material to be removed. Indeed, especially on leathers intended for high fashion, which usually have thicknesses of about 3-4 mm, such processing loss involves a significant reduction in the commercial value of the product, to the extent that it is often preferred to allocate everything to the landfill for disposal.

25 **[0005]** Although the disposal of such products is not critical in itself, it nevertheless makes the large amount of water, which can reach up to 40 L/kg of product, and of chemicals used in the processing from raw leather to tanned and finished leather, useless.

SUMMARY OF THE INVENTION

30 **[0006]** In this context, the technical task underlying the present invention is to provide a process for removing a finishing layer from finished leather which overcomes the drawbacks of the known art.

35 **[0007]** An object of the present invention is thus a process for removing a finishing layer from leather comprising the following steps:

- A. providing a finished leather comprising a surface polymeric layer disposed on said leather;
- B. subjecting the finished leather to a quick freezing;
- C. removing the surface polymeric layer from the finished leather,

40 wherein

step B is carried out by employing a cryogenic inert material.

Advantages of the invention

45 **[0008]** The process of the invention allows to remove the finishing layer from tanned and finished leathers.

50 **[0009]** Advantageously, the process according to the invention allows to remove thin finishing layers, even in the range of microns, without impairing the underlying tanned leather layer.

55 **[0010]** The removal of the finishing layer consists, therefore, in a reconditioning process allowing the basic tanned leather to be recovered without a significant reduction in the commercial value of the product. This advantage proves to be even more remarkable when the inventive process is applied to leathers with high commercial value, such as those intended for high fashion. Once the basic tanned leather has been recovered by removing the finishing layer, it can be consequently reused, for example by subjecting it to further surface finishing processes.

60 **[0011]** Thus, the inventive process fits fully in the perspective of a circular economy, since it allows to recondition and, therefore, to reuse products based on tanned and finished leather as well as the production waste thereof, otherwise allocated for disposal.

DESCRIPTION OF THE DRAWINGS

65 **[0012]**

Figure 1 shows a block diagram of the process according to the present invention which highlights the detachment of the surface polymeric layer (film) from the leather.

Figure 2 shows a diagram of an embodiment of the deposition process, wherein carbon dioxide snow is used as the cryogenic inert material. The CO₂ snow is deposited by means of a suitable sprayer on the surface of the finished leather (substrate) resulting in the removal of the surface polymeric layer.

Figures 3a and 3b illustrate two photos of a first sample of finished leather, before (3a) and after (3b) being subjected to the removal process according to the present invention, respectively.

Figures 4a and 4b illustrate two photos of a second sample of finished leather, before (4a) and after (4b) being subjected to the removal process according to the present invention, respectively.

Figures 5a and 5b illustrate two photos of a third sample of finished leather, before (5a) and after (5b) being subjected to the removal process according to the present invention, respectively.

Figures 6a and 6b illustrate two photos of the microstructure of the profile of a sample of finished leather, before (6a) and after (6b) being subjected to the removal process according to the present invention using liquid nitrogen as cryogenic inert material, respectively. Both photos were obtained using a SEM microscope with 100 µm resolution.

Figures 7a and 7b illustrate two photos of the microstructure of the upper surface, i.e.

the contact surface between the polymeric layer and the leather, of a sample of finished leather, before (6a) and after (6b) having been subjected to the removal process according to the present invention using liquid nitrogen as cryogenic inert material,

respectively. Both photos were obtained using a SEM microscope with 100 µm resolution.

Figures 8a and 8b illustrate two photos of the microstructure of the lower surface, opposed to the upper surface, of a sample of finished leather, before (8a) and after (8b) having been subjected to the removal process according to the present invention using liquid nitrogen as cryogenic inert material, respectively. Both photos were obtained using a SEM microscope with 100 µm resolution.

DETAILED DESCRIPTION OF THE INVENTION

[0013] For the purposes of the present invention, the term "comprising" does not exclude the possibility of further components and/or stages existing in addition to those expressly listed after such term; conversely, the term "consisting of" excludes the possibility of further components existing in addition to those expressly listed after such term.

[0014] For the purposes of the present invention, the term "finished leather" means a leather that has undergone finishing operations and is usable or has already been used for manufacturing a final product, such as shoes, bags, or clothes.

[0015] For the purposes of the present invention, the finished leather on which the process is carried out is a tanned leather.

[0016] The term "tanned leather" means any leather that has undergone a tanning treatment. By way of example, the tanning treatments include: chrome tanning, vegetable tanning, aldehyde tanning, synthetic tannin tanning, sulphochloride tanning, resin tanning, oil tanning.

[0017] The finished leather used in the inventive process is preferably eco-leather or vegan leather.

[0018] For the purposes of the present invention, eco-leather refers to a type of leather or hide with reduced environmental impact, meeting the requirements of the UNI 11427:2011 standard.

[0019] This definition also includes artificial leather comprising or consisting of polyester fibres, and vegan leather consisting of natural fibres, in particular cotton fibres.

[0020] As mentioned above, the object of the present invention is a process for removing a finishing layer from finished leather comprising the steps described below.

[0021] In step A of the removal process, a finished leather comprising a surface polymeric layer disposed on said leather is provided.

[0022] Preferably, the finished leather has a thickness of between 1 and 6 mm, preferably between 1 and 3 mm, preferably of 2 mm, and the process can be carried out on leathers with a surface area between 0.5 m² and more than 1 m².

[0023] Preferably, the finishing surface polymeric layer has a thickness of between 1 and 20 microns, preferably between 1 and 18 microns, preferably between 1 and 10 microns.

[0024] Preferably, the surface polymeric layer comprises a mixture of different polymers, preferably polyurethanes and/or acrylic resins.

[0025] Preferably, when the finished leather is vegan leather, the surface polymeric layer comprises polymer matrices, preferably a polyester matrix.

[0026] In step B of the removal process, the finished leather is subjected to a quick freezing.

[0027] Advantageously, the quick freezing of the finished leather causes the surface polymeric layer to break and detach from the leather. This is essentially ascribable to the different glass transition temperature and the different coefficient of thermal expansion of the polymeric layer and the leather, determined by the complex structural divergences of the materials of the two layers. Indeed, the quick-freezing leads to a stress pressure state in the tanned leather and to an expansion stress state in the surface polymeric layer (Figure 1).

[0028] The removal process according to the present invention is characterized in that step B is carried out by employing a cryogenic inert material.

[0029] Preferably, the cryogenic inert material is selected from: liquid nitrogen, dry ice, or carbon dioxide snow. Preferably, the cryogenic inert material is liquid nitrogen.

[0030] Accordingly, step B of the removal process is preferably carried out at a temperature below -10 °C, preferably ranging from -210 °C to -10 °C, preferably ranging from -198 °C to -78 °C, preferably of -198 °C.

[0031] Preferably, the weight ratio of the amount of cryogenic material used in stage B to that of finished leather is between 0.5 and 2, preferably of 0.75.

[0032] This ratio is justified by the energy balance in which the latent heat removed by the evaporation of the cryogenic fluid is balanced by the sensible heat required for cooling, as expressed by the following equation:

$$m_p C_p \Delta T = m_{fc} \Delta H_{ev}$$

where m_p and m_{fc} are the masses of the leather and the cryogenic fluid; C_p , typically in the order of magnitude of 1500 J/kgK, is the specific heat of the tanned leather; ΔT and ΔH_{ev} are the required temperature reduction in the leather, typically of about a hundred Celsius degrees, and the evaporation latent heat of the cryogenic fluid, typically 198000 J/kg, respectively.

[0033] Preferably, when the cryogenic inert material is liquid nitrogen, step B comprises pouring said cryogenic inert material on the finished leather. Preferably, this step consists in spraying the liquid nitrogen in jets onto the finished leather, as highlighted in Figure 2, the difference being that the outflow rate required using liquid nitrogen is lower than when using carbon dioxide snow.

[0034] During the application of liquid nitrogen, the finished leather is preferably moved. Handling is achieved by means of a suitable conveyor belt system, where the leather is transported horizontally, the finishing polymeric layer being applied on the leather, which in turn contacts the conveyor belt.

[0035] Preferably, when the cryogenic inert material is dry ice, step B comprises contacting the cryogenic inert material with the finished leather.

[0036] Preferably, this step consists in loading the dry ice and the finished leather into a designated ball mill, or in rubbing the dry ice directly on the finished leather surface, until the detachment of the polymeric layer is detached.

[0037] Preferably, when the cryogenic inert material is carbon dioxide snow, step B comprises depositing said cryogenic inert material on the surface polymeric layer of the finished leather.

[0038] Preferably, this step consists in spraying jets of carbon dioxide snow, preferably by means of a suitable spraying device provided with a nozzle, in which the snow is placed under pressure. As a result of the lamination, the carbon dioxide snow solidifies, generating particles 1-2 microns thick. These particles are sprayed onto the finished leather surface and vaporize when impacting on the same, absorbing the sublimation heat that they subtract from the leather surface which, in turn, cools. The carbon dioxide snow cooling reduces the surface polymeric layer to chips.

[0039] In step C of the process, the surface polymeric layer is removed from the finished leather.

[0040] Preferably, when the cryogenic inert material is liquid nitrogen, the surface polymeric layer is removed while maintaining the finished leather from step B subjected to quick cooling.

[0041] Preferably, when the cryogenic inert material is dry ice, the surface polymeric layer from step B is removed by applying an air jet on the finished leather subjected to quick cooling

[0042] Preferably, the air jet is applied after a time ranging from a few seconds to one minute has elapsed, preferably within 30 seconds after the dry ice is applied.

[0043] Preferably, when the cryogenic inert material is carbon dioxide snow, the removal of the surface polymeric layer occurs directly following the application of the cryogenic inert material on the surface polymeric layer of the finished leather. Indeed, the carbon dioxide snow particles when impacting the leather surface, pass from a solid state to a gaseous state. During this sublimation process, the gas formed has a volume about 1.000 times larger than that of the solid particles. This expansion moves the surface polymeric layer, reduced to chips, away from the leather (Figure 2).

[0044] Preferably, when the finished leather is moved on a conveyor belt, the removal of the surface layer also occurs by means of a suitable suction system.

[0045] Preferably, in addition to the suction system, there can also be a system of rotating brushes, placed above the finished leather. Advantageously, the rotating brushes are able, by friction with the leather surface, to remove even the smallest residues of the polymeric layer.

Experimental part

[0046] By comparing Figures 3a vs. 3b, 4a vs. 4b, and 5a vs. 5b, it is clear that the removal process according to the present invention allows to remove completely only the thin surface polymeric layer or finishing layer, the surface of which appears smoother and more homogeneous, while leaving the leather structure, the surface of which appears coarser and rougher, substantially unaltered.

[0047] In this regard, the thickness values before (initial) and after (final) the treatment by the inventive process are reported below in Table 1 for samples 1, 2, 3, depicted in Figures 3a-3b (sample 1), 4a-4b (sample 2), and 5a-5b (sample 3), respectively.

Table 1: "initial and final thickness of 3 finished leather samples"

Sample	Initial thickness (mm)	Final thickness (mm)	Removed thickness (initial thickness - final thickness) (mm)
1	1.64	1.54	0.10
2	1.56	1.36	0.20
3	1.29	1.11	0.18

Microscopic analysis (SEM)

[0048] To confirm what has been discussed above, scanning electron microscopy (SEM) analysis were conducted on a sample of finished leather, photographing the structure of the sample before and after the application of the removal process according to the present invention.

[0049] By comparing Figures 6a vs 6b, 7a vs 7b, and 8a vs 8b, characterized by similar levels of magnification, it is clear that the process according to the present invention allows to remove only the thin finishing layer, which exhibits a definitely finer and more homogeneous structure (Figures 6a and 7a), while leaving the leather, which exhibits a definitely coarser and heterogeneous structure instead, substantially unaltered. (Figures 8a-8b).

Claims

1. A process for removing a finishing layer from leather, comprising the following steps:

- A. providing a finished leather comprising a surface polymeric layer disposed on said leather;
- B. subjecting the finished leather to a quick freezing;
- C. removing the surface polymeric layer from the finished leather,

wherein

step B is carried out by employing a cryogenic inert material.

2. The process according to claim 1, wherein step B is carried out at a temperature below -10 °C, preferably ranging from -210 °C to -10 °C, preferably ranging from -198 °C to -78 °C, preferably of -198 °C.

3. The process according to claim 1 or 2, wherein the finished leather is eco-leather.

4. The process according to any one of claims 1 to 3, wherein the surface polymeric layer comprises a mixture of different polymers, preferably polyurethanes and/or acrylic resins.

5. The process according to any one of claims 1 to 4, wherein the cryogenic inert material is selected from: liquid nitrogen, dry ice, or carbon dioxide snow, preferably liquid nitrogen.

6. The process according to any one of claims 1 to 5, wherein, when the cryogenic inert material is liquid nitrogen,

step B comprises pouring, preferably spraying said cryogenic inert material on the surface polymeric layer of the finished leather.

7. The process according to any one of claims 1 to 6, wherein, when the cryogenic inert material is dry ice, step B comprises contacting said cryogenic inert material with the finished leather.
8. The process according to any one of claims 1 to 6, wherein, when the cryogenic inert material is carbon dioxide snow, step B comprises depositing said cryogenic inert material on the surface polymeric layer of the finished leather.

Fig. 1

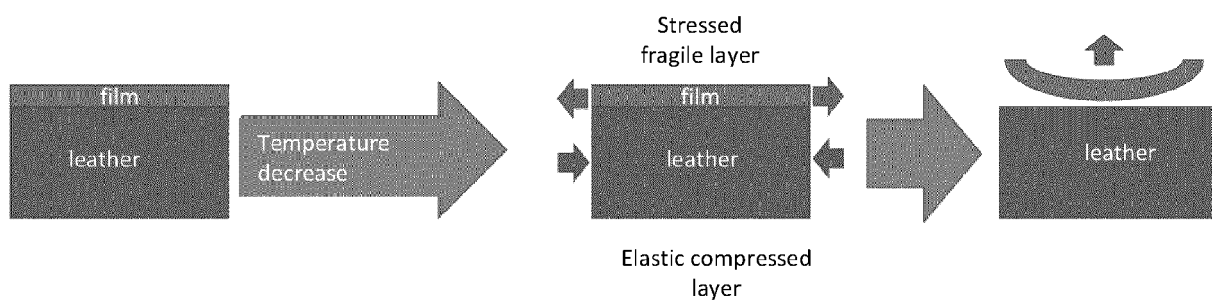


Fig. 2

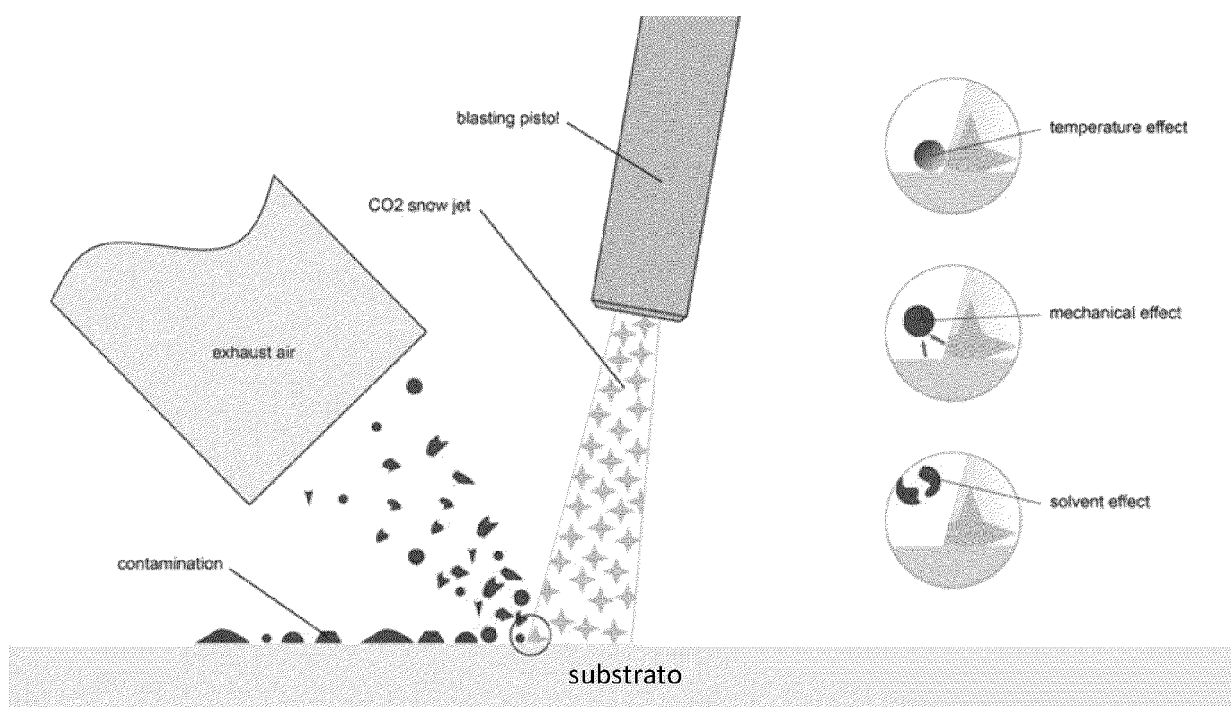
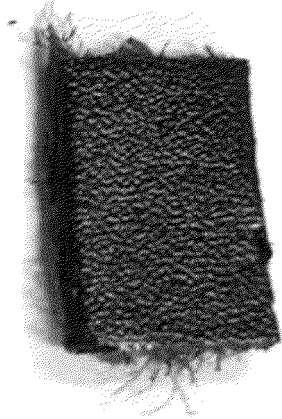
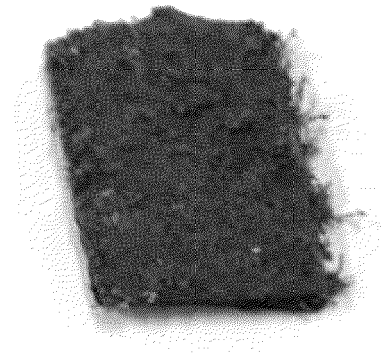


Fig. 3a



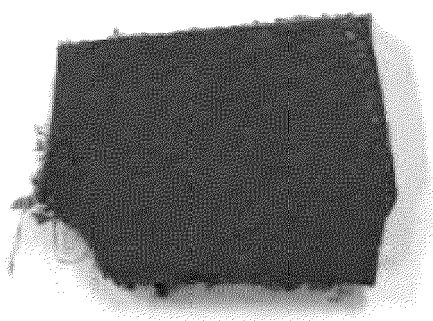
Before

Fig. 3b



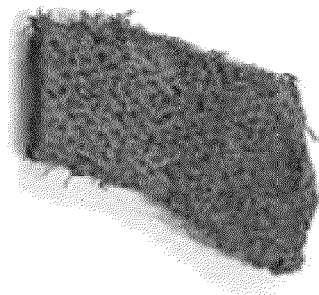
After

Fig. 4a



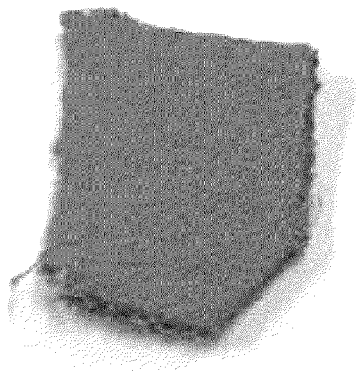
Before

Fig. 4b



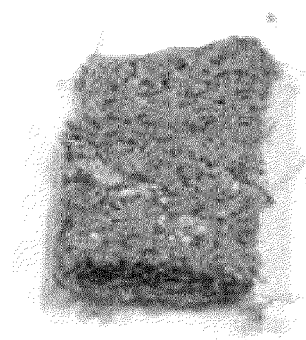
After

Fig. 5a



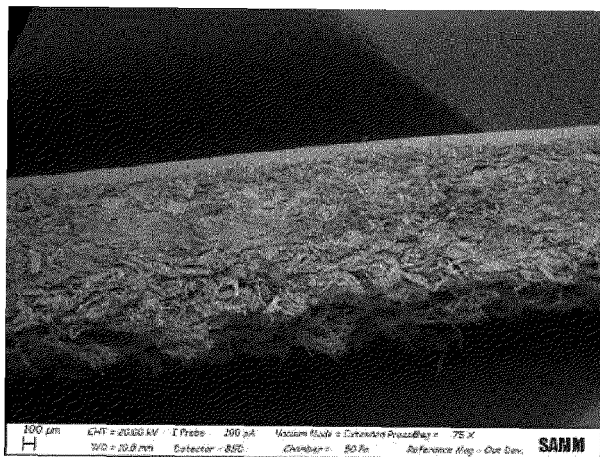
Before

Fig. 5b



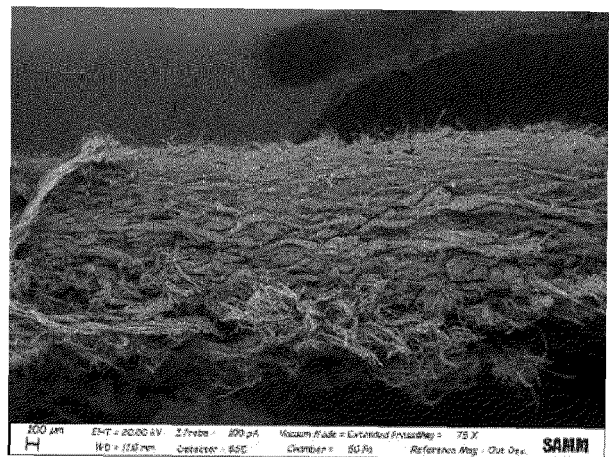
After

Fig. 6a



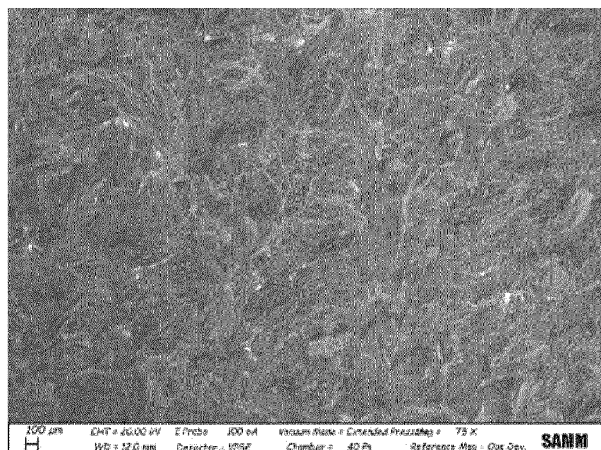
Before

Fig. 6b



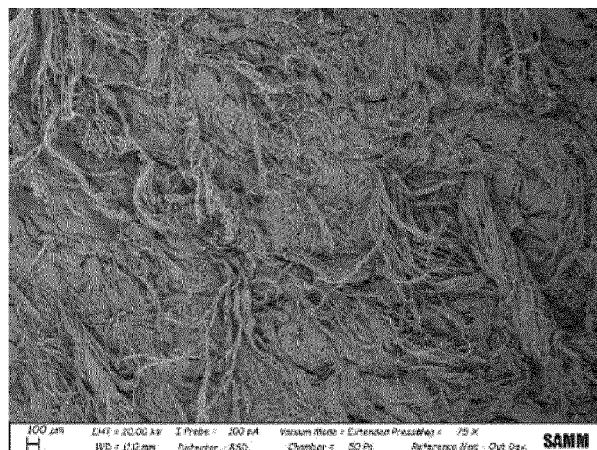
After

Fig. 7a



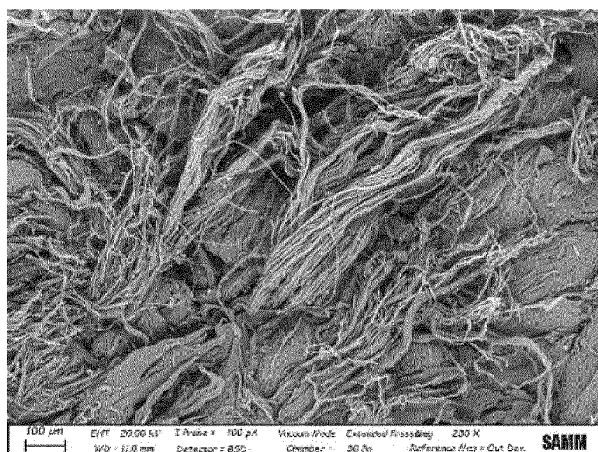
Before

Fig. 7b



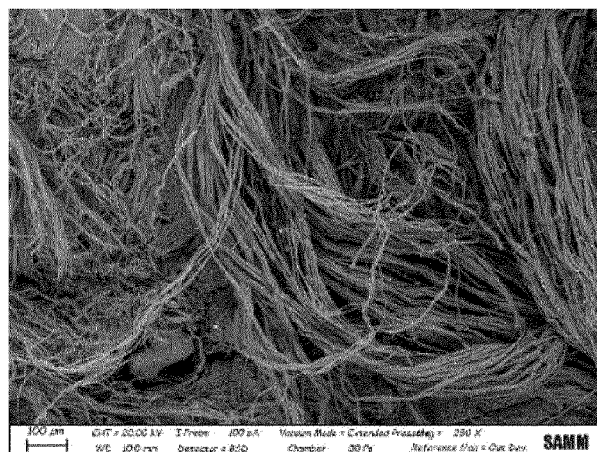
After

Fig. 8a



Before

Fig. 8b



After



EUROPEAN SEARCH REPORT

Application Number

EP 24 16 7883

5

10

15

20

25

30

35

40

45

50

55

1

EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	DE 20 2014 101465 U1 (TQ SYSTEMS GMBH [DE]) 3 April 2014 (2014-04-03)	1-5,7,8	INV.
A	* paragraphs [0001] - [0017], [0034] - [0045], [0066] - [0078]; claims; figures *	6	C14B1/44 B24C1/00
Y	----- CN 110 565 389 A (XINGYE LEATHER TECH CO LTD) 13 December 2019 (2019-12-13)	1-5,7,8	
A	* paragraphs [0006] - [0011], [0002] - [0021]; claims; figures *	6	
A	----- MÁSA VÍTEZSLAV ET AL: "Industrial use of dry ice blasting in surface cleaning", JOURNAL OF CLEANER PRODUCTION, ELSEVIER, AMSTERDAM, NL, vol. 329, 12 November 2021 (2021-11-12), XP086891778, ISSN: 0959-6526, DOI: 10.1016/J.JCLEPRO.2021.129630 [retrieved on 2021-11-12] * the whole document *	1-8	
	-----		TECHNICAL FIELDS SEARCHED (IPC)
			C14B B24C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 22 July 2024	Examiner Clivio, Eugenio
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	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 24 16 7883

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22 - 07 - 2024

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 202014101465 U1	03 - 04 - 2014	NONE	

CN 110565389 A	13 - 12 - 2019	NONE	

15

20

25

30

35

40

45

50

55

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82