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(54) LEATHER WITH SELF-CLEANING PROPERTIES AND RESISTANCE TO HEAT/FIRE AND METHOD OF OBTAINING THEREOF

(57) The invention relates to leather for furniture and automotive upholstery and protective footwear, surface finished with titanium dioxide nano particles doped with 10% silica with an average particle size of 46 nm and with self-cleaning properties and improved resistance to heat transmission and combustion. The process for obtaining leather with self-cleaning properties and resistance to heat/fire consists in applying the base coat containing 0.05-10% titanium dioxide nano particles (% relative to the amount of binder) doped with 10% of silica which are dispersed in an equal amount of polyethylene glycol 600 and, according to another variant, 0.01-15% sodium polyacrylate, by mechanical stirring for 10 minutes, followed by sonication for 5 minutes, with pigment paste based on macro titanium dioxide, water and acrylic binder. This composition is applied by spraying in successive coats with intermediate drying and final pressing at 110°C and 20 kgf, followed by fixation with nitrocellulose lacquer in successive coats, with intermediate drying and final pressing in the same conditions. Self-cleaning properties are provided through photocatalytic degradation of organic dirt under the influence of ultraviolet and visible light and resistance to heat transfer and combustion.

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Description

[0001] The invention relates to leather with surface properties such as self-cleaning and resistance to heat/fire, properties highly required for leather upholstery and protective footwear, and method of obtaining thereof.

[0002] Materials and methods of waterproofing leather surface are known, allowing water and dirt to not adhere to the surface of leather. Thus, in EP 1789595 A1 patent, super-hydrophobic effects are achieved, in conjunction with self-cleaning properties, by polishing the surface of leather treated with classic agents based on commercial waterproofing materials. The disadvantage is that the method uses expensive treatment materials, which must penetrate at least 30% of the leather cross-section, and requires polishing the surface, which limits the possibility of using natural grain leather.

[0003] Another patent, WO 96/04123**,** proposes the use of pyrogenic silica in nano form on the surface of materials such as leather or textiles. The disadvantage is that the method changes the appearance of leather surface, which limits its industrial applicability.

[0004] Patent US 20130078451 A1 shows a process for manufacturing leather used to cover surfaces, similar to a rug, with antimicrobial properties and resistance to water and wear, improved by coating the surface with silver and silica nano particles. The disadvantage of the method consists in the application of the process restricted to this leather assortment only, suggesting a stiffening of the surface and limited scope. Patent literature does not report the application of nanomaterials with photocatalytic functions to break down dirt that reaches the leather surface. Most patents combine silicone and fluorosilicone materials with nano materials to increase surface tension and reject dirt particles that would adhere, self-cleaning taking place through the formation of spherical water droplets, with capacity to roll on the inclined leather surface and drag soluble dirt.

[0005] Patent CN 101412869 B shows nano pigments based on nano titanium dioxide, nano zinc oxide or nano silica and method of using them for surface finishing of natural leather, thus producing leather with antibacterial properties, resistance to fire and UV radiation. The process presented in the patent has the disadvantage that the leather surface does not have any self-cleaning properties when in contact with dirt.

[0006] The technical problem solved by the invention relates to natural leather with photocatalytic self-cleaning properties of the surface, under the influence of UV and visible light, with resistance to heat transfer and improved combustion behavior and the process for obtaining thereof.

[0007] Leather with self-cleaning properties and resistance to heat/fire has the following advantages:

- it is multifunctional and can be used to make upholstery for furniture, cars, planes or protective footwear for firefighters, metallurgists, etc. because it provides protection from dirt and fire-associated risks;
- no halogenated organic compounds (currently used) are used for fireproofing, which do not ensure a durable treatment, as they are volatile, and are toxic to users and contribute to the greenhouse effect;
- it is more durable because organic dirt that adheres to the surface is decomposed under visible or ultraviolet light, an unpatented property to date for natural leather;
- it allows reducing costs for maintenance and pollution by organic solvents used in dry cleaning and reconditioning, especially for increasingly numerous white and light coloured varieties that are most vulnerable to dirt.

[0008] Leather with self-cleaning properties and resistance to heat/fire is made by coating the surface of leather by classic spraying method using film-forming composites containing titanium dioxide nano particles doped with 10% silica in concentration from 0.01 to 6 g/100cm^2. Titanium dioxide nano particles doped with 10% silica are obtained by hydrothermal method, at a pressure of 40 atmospheres and a temperature of 200°C and have an average particle size of 46 nm, determined by transmission electron microscopy.

[0009] Self-cleaning properties were assessed by staining the surface of finished leather with titanium dioxide nano particles doped with 10% silica with model organic dirt, namely methylene blue dye ($C_{16}H_{18}ClN_3S \cdot 3H_2O$) and ball-point pen ink, and through exposure to UV light (λ = 365 nm) using a VL 204 lamp and to visible light using a 500W halogen lamp, according to methods found in literature. As control samples, leather surfaces treated with undoped titanium dioxide nano particles and finished leather surfaces without nano particles were exposed under identical conditions. The results are shown in Table 1 and show that under visible light, self-cleaning is faster than under ultraviolet light, which is an important advantage compared to the treatments with undoped titanium dioxide nano particles with photocatalytic activity only in ultraviolet light. These properties are an important advantage because ultraviolet light is 4 to 6% of visible light, so the functionality of self-cleaning effects is much higher. Self-cleaning takes place 3 times faster when treated leather is exposed to visible light, compared to leather exposed to ultraviolet light (Table 1). Self-cleaning in the visible light range is due to the action of the dopant on the electronic structure of nano titanium dioxide, affecting the shift towards the visible absorption bands thereof. As a result, photocatalytic reactions take place, which, in the presence of water molecules, generate oxidative species that break down organic dirt adhering to the leather surface. Photocatalytic effects of nano titanium dioxide on the surface of leather are improved by doping it with 10% silica as compared to those of finished leather with undoped titanium dioxide and finished leather without nano particles (Table 2).

Table 1-Bovine leather surface treated with titanium dioxide nanoparticles doped with 10% silica with self-cleaning properties under UV and visible light.

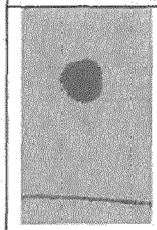
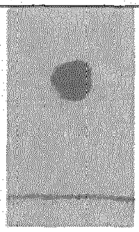
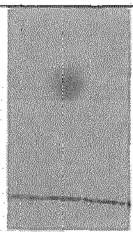
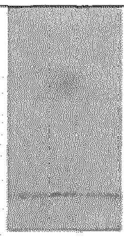
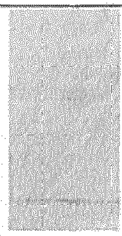
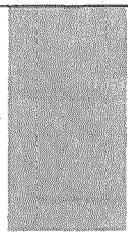
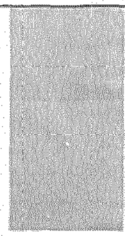
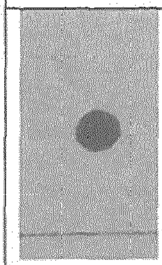
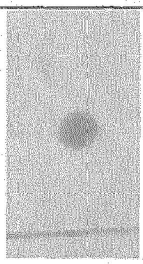
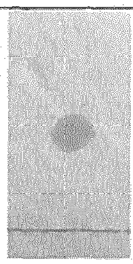
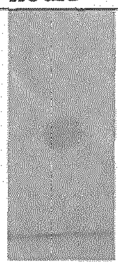
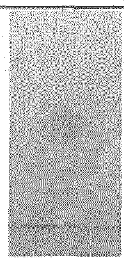
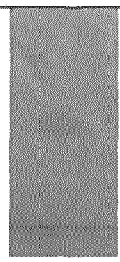
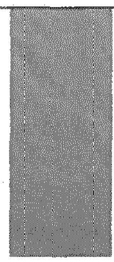
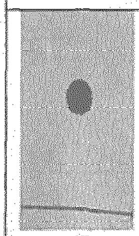
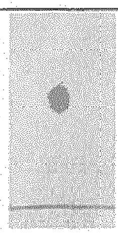
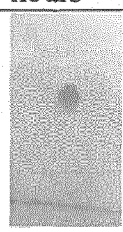
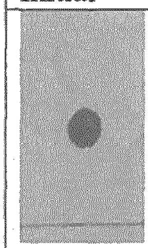
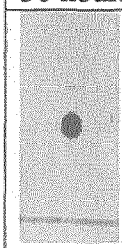
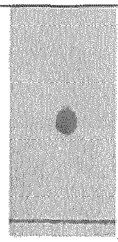
Initial	3 hours	30 hours	60 hours	100 hours	150 hours	214 hours
						
Exposure to UV light						
Initial	3 hours	5 hours	10 hours	20 hours	30 hours	70 hours
						
Exposure to visible light						

Table 2-Conventionally finished bovine leather surface exposed to UV and visible light.

Initial		150 hours	214 hours
			
Exposure to UV light			
Initial		30 hours	70 hours
			
Exposure to visible light			

[0010] Heat resistance was determined in accordance with EN 702:2003 and indicated a contact heat transmission threshold upon exposure to a temperature of 250°C for 24.11 seconds for the leather treated with titanium dioxide nano particles, doped with 10% silica, compared to 21.41 seconds recorded for untreated leather. Combustion behavior was evaluated according to the methods described in EN ISO 15025:2006 and indicated an afterglowy time of 10 seconds for treated leather compared to 250 seconds for untreated skin by exposure to combustion for 10 seconds.

[0011] The method of manufacturing bovine leather with self-cleaning properties and resistance to heat/fire consists in integrating titanium dioxide nano particles doped with 10% titanium dioxide in the base finishing composite, containing acrylic binders, pigment paste and water, by dispersing them using polyethylene glycol 600, with or without sodium polyacrylate by mechanical stirring and ultrasonication. The coating is classically applied, manually, by spraying, or in the automatic finishing booth, in successive layers, with intermediate drying, by pressing the base coat and final coating before fixing the base coat with nitrocellulose lacquer coats, which finally polymerize by pressing.

[0012] The advantages of the manufacturing process of leather with self-cleaning properties and resistance to heat/fire are listed below:

- It is a simple and efficient method that does not require additional operations compared to the classic process and allows the elimination of fire retardant or hydrophobic volatile organic compounds;
- It uses small amounts of nanomaterials that make the leather surface versatile and durable;
- The method does not stiffen the surface and does not limit the use for various kinds of leather, from rigid to soft ones;

[0013] The following are the 4 embodiments for bovine leather with self-cleaning properties and resistance to heat/fire.

[0014] Embodiments 1 and 2 show the reference procedures for finishing leather without nano particles and finishing with undoped titanium dioxide nano particles, and Embodiments 3 and 4 show finishing processes using titanium dioxide nano particles doped with 10% silica.

Embodiment 1

[0015] Leather tanned with basic chromium salts and retanned using a conventional process (with chromium salts and synthetic tanning agents) is finished in white colour using polymeric composites based on acrylic binders, which form the base layer and then fixed with nitrocellulose lacquer, according to the procedure described below. Basecoat finishing consists in applying an aqueous emulsion of acrylic polymer with a concentration of 250 g/L, which is mixed with 110 g/L pigment paste based on macro titanium dioxide, water up to 1L, and is applied in 4 coats by spraying and intermediate drying, followed by pressing at 110°C and 20 kgf. Next 2 additional base coats are applied with intermediate and final free drying. Two final fixing coats are applied by spraying a nitrocellulose lacquer in a concentration of 850 g/L with intermediate drying between coats and final pressing at 110°C and 20 kgf.

Embodiment 2

[0016] The base coat containing doped titanium dioxide nanoparticles with an average particle size of 25 nm, is prepared by mixing an amount of 0.05-10% (% relative to the amount of binder) with an amount equal to the mass of polyethylene glycol 600 nano particles, 110 g/L pigment paste based on macro titanium dioxide, water up to 1L and 250 g/L acrylic binder, followed by mechanical stirring for 30 minutes and 5 minutes stirring by ultrasonication at 50/60 Hz. Further, the application of the finish is the same as that described in Embodiment 1.

Embodiment 3

[0017] The base coat containing titanium dioxide nanoparticles doped with 10% silica, with an average particle size of 46 nm, is prepared by mixing an amount of 0.05-10% (% relative to the amount of binder) with an amount equal to the mass of polyethylene glycol 600 nano particles, 110 g/L pigment paste based on macro titanium dioxide, water up to 1L and 250 g/L acrylic binder, followed by mechanical stirring for 30 minutes and 5 minutes stirring by ultrasonication at 50/60 Hz. Further, the application of the finish is the same as that described in Embodiment 1.

Embodiment 4

[0018] The base coat containing titanium dioxide nanoparticles doped with 10% silica, with an average particle size of 46 nm, is prepared by mixing an amount of 0.05-10% (% relative to the amount of binder) with an amount equal to the mass of polyethylene glycol 600 nano particles and to 0.01-15% sodium polyacrylate (% relative to the amount of nano particles) 110 g/L pigment paste based on macro titanium dioxide, water up to 1L and 250 g/L acrylic binder, followed by mechanical stirring for 30 minutes and 5 minutes stirring by ultrasonication at 50/60 Hz. Further, the application of the finish is the same as that described in Embodiment 1.

Claims

1. Bovine leather with self-cleaning properties, resistance to heat/fire, **characterized in that** the leather surface is coated with 0.01-6 g/100cm^2 titanium dioxide nano particle doped with 10% silica, with an average particle size of 46 nm which exhibit photocatalytic decomposition of organic dirt under the influence of UV and visible light, improved resistance to heat transfer and afterglow time compared to the leather finished without nano particles.

2. A method for manufacturing leather with self-cleaning properties and resistance to heat/fire, **characterized in that** 0.05-10% titanium dioxide nano-particles (% relative to the amount of binder) doped with 10 % silica, with an average particle size of 46 nm, are added to the base coat in leather surface finishing by mechanical stirring for 10 minutes, followed by 5 minutes of ultrasonic treatment, with equal amounts of polyethylene glycol 600, 110 g/L pigment paste based on macro titanium dioxide, water up to 1 L and 250 g/L acrylic binder, applied by spraying in 4 successive coats, with intermediate drying and final pressing at 110°C and 20 kgf, followed by 2 coats of finish with intermediate and final free drying and fixing with 2 coats of nitrocellulose lacquer emulsion with the concentration of 850 g/L and final pressing at the same parameters.

3. A method for manufacturing leather with self-cleaning properties and resistance to heat/fire, **characterized in that** 0.05-10% titanium dioxide nano-particles (% relative to the amount of binder) doped with 10 % silica, with an average particle size of 46 nm, are added to the base coat in leather surface finishing by mechanical stirring for 10 minutes, followed by 5 minutes of ultrasonic treatment, with equal amounts of polyethylene glycol 600, 0.01-15% sodium polyacrylate, 110 g/L pigment paste based on macro titanium dioxide, water up to 1L and 250 g/L acrylic binder, applied by spraying in 4 successive coats, with intermediate drying and final pressing at 110°C and 20 kgf, followed by 2 coats of finish with intermediate and final free drying and fixing with 2 coats of nitrocellulose lacquer emulsion with the concentration of 850 g/L and final pressing at the same parameters.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 46 4008

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	PETICA A. ET AL.: "Doped TiO2 nanophotocatalysts for leather surface finishing", JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH, vol. 12, no. 6, 20 August 2015 (2015-08-20), pages 1153-1163, XP002764756, Springer.com DOI: 10.1007/s11998-015-9711-2 * the whole document * -----	1-3	INV. C14C11/00 C14C13/00 C14C9/00
A	DATABASE WPI Week 201556 Thomson Scientific, London, GB; AN 2015-420494 XP002764757, & CN 104 610 832 A (WANG Y) 13 May 2015 (2015-05-13) * abstract * -----	1-3	
A,D	DATABASE WPI Week 200946 Thomson Scientific, London, GB; AN 2009-H89744 XP002764758, & CN 101 412 869 A (UNIV SICHUAN) 22 April 2009 (2009-04-22) * abstract * -----	1-3	TECHNICAL FIELDS SEARCHED (IPC) C14C
A	GB 1 216 479 A (NIPPON PAINT CO LTD [JP]) 23 December 1970 (1970-12-23) * page 1, line 11 - page 3, line 106 * * page 2; examples 1-6; tables 1,2 * -----	1-3	

1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	6 April 2017	Neugebauer, Ute

CATEGORY OF CITED DOCUMENTS

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06-04-2017

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			GB	1216479 A	23-12-1970

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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- WO 9604123 A **[0003]**
- US 20130078451 A1 **[0004]**
- CN 101412869 B **[0005]**