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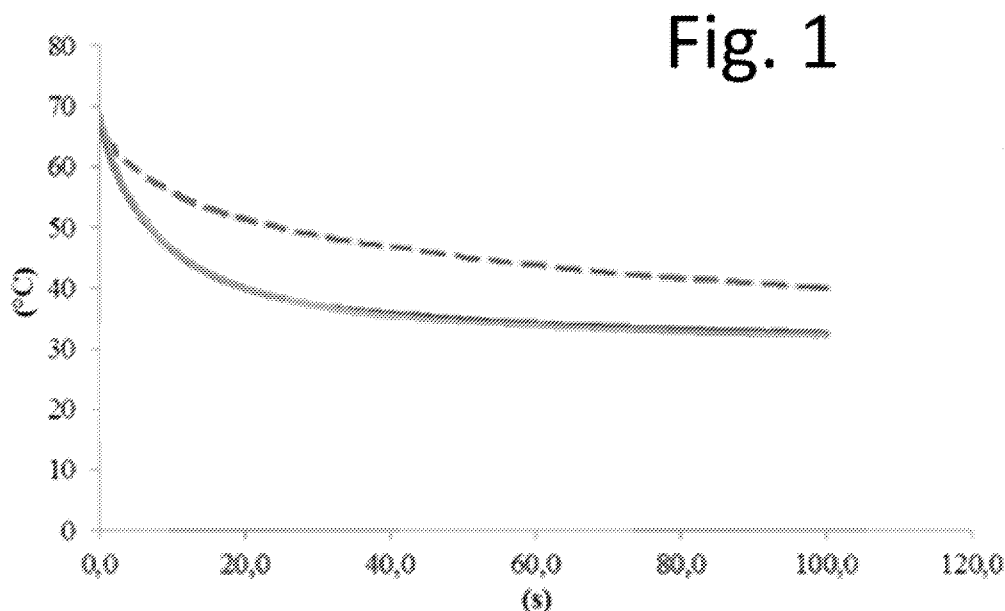
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(54) Title: THERMALLY DISPERSING AND ELECTRICALLY CONDUCTIVE PROCESSED LEATHER



(57) Abstract: A thermally conductive modified synthetic or natural leather material adapted for a lining of a product, in particular for the passenger compartment of a vehicle, comprising a thermally conductive agent including graphene particles; wherein - at least a portion of the material is impregnated with the thermally conductive agent comprising graphene particles at a sufficient concentration to provide thermal conductivity in the modified material; the modified material having a thermal decay of 29% or more starting from 0 70°C at ambient temperature of 21°C in less than 20 seconds.



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Thermally dispersing and electrically conductive processed leather

DESCRIPTION

5 **TECHNICAL FIELD**

The present invention relates to a treated leather to achieve thermal dispersion by means of a relatively quick cooling after exposure to a heat source and a good electrical conductivity.

STATE OF THE ART

10 Leather is used in many industries and products. In some cases, such as for example in the automotive industry, requirements for acceptance of an original equipment supply are quite demanding. Indeed, in such an industry, leather is applied as an external layer or lining to many friction-wearable elements, e.g. steering wheel, seats, front and rear door internal handles and the like. In such a
15 case, it is important that leather preserves a soft touch surface over the working life of the vehicle and, in the particular case of seats, a relatively high elasticity and softness in order to reduce or avoid cracks after a number of deformations due to seating of the user.

Similar requirements are also common in other industries, at least for high
20 end products, such as in the fashion industry, e.g. in wearable products such as shoes, watch straps, dresses; or in accessories such as backpacks, purses and other leather goods such as a cover for smartphone or the like.

Increasing sophistication of the consumer pushes a traditional industry such as that of leather goods to provide leather with improved performances also
25 with respect to aspects that are additional to more traditional waterproofing, wear resistance, durability, environment friendliness of the manufacturing

process.

Other leather goods that need a high heat dispersion are safety footwear used in environments where there are heat sources, such as firemen's clothing, or protective clothings that are worn even under strong solar radiation, such as
5 biker suits.

SCOPE AND BRIEF DESCRIPTION OF THE INVENTION

The purpose of the present invention is to provide a new leather able to provide increased performances over a wide range of parameters and needs.

The purpose of the present invention is achieved by a leather processed to
10 provide increased thermal dissipation by impregnating, i.e. including in the voids and ductuli of a stabilized collagen matrix, crust leather with graphene particles.

In the following the term particles will not be limiting and will include various shapes, such as platelets, particles, fibers and corresponding mixtures.

15 The thus obtained processed leather is characterized by increasing temperature decay after exposure to a heat source, it provides a better feeling to the user when part of the leather product is exposed for a long time to a heat source. In car industry, a leather-lined dark-colored steering wheel or passenger seat exposed for a long time to sunlight and hot weather, e.g. after a week-long
20 parking in an open area, will keep a relatively low temperature compared to that of e.g. metallic parts inside the cabin in order to give the user an improved feeling if there is no time available to fully cool down the inner environment of the vehicle. The processed leather is characterized by a relative high heat dispersion that provides for a faster cool down when the vehicle door is opened and/or the
25 cooling system of the vehicle is switched on.

According to an embodiment, the leather comprises electrically conductive

particles, such as platelets and/or fibers added to a finishing layer and/or an adhesive layer in order to decrease electrical resistivity and improve the processed leather versatility. This generates a particularly polyvalent new material providing, at once, both improved thermal decay and electric conductivity. In particular, the bulk impregnation by graphene for thermal decay functions as a bypass electric conductor in case surface conductivity is negatively impacted e.g. because the finishing layer becomes worn in use or damaged by e.g. scratches. Therefore, surface conductivity is kept at good levels over the entire working life of the product.

10 Preferably, such particles are of graphene and even more preferably are the same particles used for impregnation of the crust leather.

Other advantages and features of the present invention are discussed in the description and cited in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWING

15 The invention will be herein described based on non-limiting embodiments and tests shown for explanatory purposes in the attached drawing, which shows a graph to compare a thermal decay for a leather material according to the invention (solid line) and a standard leather material (dashed line).

DETAILED DESCRIPTION OF THE INVENTION

20 Leather is obtained in a process comprising a first phase where the hide is treated to lose hair, sub-cutaneous tissue, residual flesh and fat remnants and is tanned to become wet blue or wet white (leather material in a wet condition as result of an intermediate stage of manufacturing), i.e. a stabilized collagen matrix in the wet state that is resistant to putrefaction and can be used as a substrate for
25 subsequent phases such as re-tanning, fat-liquoring and dyeing. To stabilize the collagen matrix, tanning agents are used, including trivalent chromium salts to

provide the so-called wet-blue, or aluminum, titanium, zirconium, aldehydes, vegetable or synthetic tannins, 2-halo-4,6-dialkoxy-1,3,5-triazines, as discussed e.g. WO2016103185 and their quaternary ammonium salts, including 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) as disclosed in WO2015044971 in the name of the applicant, to provide the so-called wet-white. After tanning, the wet blue or wet white leather material is subjected to re-tanning and fatliquoring wet processes in order to achieve the correct softness, dimensional stability and provide the leather in the crust condition (dry leather with article-related bulk properties to produce e.g. suede articles).

10 It is possible to provide additional treatments including coloring by tumbling in a tumbling drum, using one or more of the following formulations in the presence of water: dyestuffs, ionic additives, pH buffers, fastness agents.

Further treatments, which may be applied to colored or non-colored crust include finishing and, in particular, one or more of coating, embossing, ironing, etc. A general example of a finishing macro-phase comprises a step of applying one or more finishing treatments to the crust and a final phase of surface drying.

15 According to the present invention, after tanning and before finishing, i.e. during the crust forming, the collagen matrix is impregnated with particles and/or fibers of graphene in order to provide a crust having increased thermal conductivity of the bulk and providing improved, i.e. steeper, thermal decay with respect to un-treated crust.

The method to obtain a thermally conductive modified material according to the invention is a process comprising the step of:

25 - impregnating the leather material to be treated with an aqueous bath, preferably comprising no more than 6% in dry weight of graphene particles / weight of leather material to be treated, as a thermally conductive agent,

preferably between 2.5-5%;

- tumbling in a tanning drum;

wherein the thus obtained leather material has a thermal decay of 29% or more starting from 70°C at ambient temperature of 21°C in less than 20 seconds.

5 In the method according to the invention, during the impregnation in the aqueous bath, no adhesive is provided to bind the graphene particles to the material.

The thus obtained thermally conductive modified material is adapted for a lining of a product, in particular for the passenger compartment of a vehicle

10 The material is selected in the group of colored or non-colored crust, in particular split crust, natural or synthetic leather, e.g. alcantara®. A suitable temperature to perform the method of the invention is 55-60°C.

The presence of at least one of the following components can improve the method:

- 15 - one or a mixture of adhesives within the bath, added in amounts of no more than 20 % by weight of leather material to be treated, preferably Baytingan Bottom 43158-S. Preferably, graphene particles are not pre-mixed with the adhesive to avoid excessive viscosity of the latter;
- 20 - one or a mixture of surfactants and penetrating agents, such as Retanal HD or Coramil GN;
- the use as an ingredient for the graphene particle-based compound to be added to the processing bath, of graphene particles in liquid form comprising a surfactant (no more than 2% wt.); preferably, such liquid form is such that graphene particles are more than 90% wt.

25 Graphene particles and/or platelets and/or fibers have such a dimension to be trapped inside voids and ductuli of the collagen matrix during

impregnation. Furthermore, graphene impregnates through a substantially physical action of drum rotation. Therefore it was found that it is possible to maintain all other process parameters, e.g. bath temperature (from 22°C (24h) to 55°C (6h), then 60°C (3h)), drum rpm (from 2 to 50 rpm) etc. normally used
5 during processing in a drum. It is also possible to add graphene during a known process step, such as re-tanning and/or fatliquoring, without altering the relevant process parameters, such as temperature, pH, rotation speed and other usual process parameters.

The pH can be adjusted by adding an acid component. Suitable acids can be
10 chosen among: formic acid, acetic acid, lactic acid, phosphoric acid and other weak acids. The function of the acid is not specific, as it is added with the sole purpose of lowering the pH up to the desired value.

According to an embodiment of the present invention, impregnation with graphene particles and/or fibers is provided in a bath, in particular a water bath.
15 The bath may preferably comprise addition of an adhesive, such as for example vinyl-based adhesive, in order to improve the stability over time of adhesion of the particles and/or fibers to the collagen matrix. In particular, impregnation may be a separate bath after tanning, which may be before or after a re-tanning and/or fatliquoring bath, or graphene particles may be added together with re-
20 tanning and/or fatliquoring additives to obtain crust. Preferably, graphene is added after re-tanning and/or fatliquoring and/or dyeing so as to help the retention of the particles.

It was found that there is no need for an intermediate drying of the tanned collagen before graphene impregnation. As graphene impregnation general
25 conditions may be those of retanning, dyeing and fatliquoring, a drum is generally partially filled with water and the bath temperature is at least 20°C] by

either partially filling the drum with water at such a temperature or by heating water in the drum. Preferred operative conditions are 22°C after graphene addition for 24 h, then 55°C for 3 h. The rotation of the drum favors impregnation but, depending on the case, an adhesive may be added.

5 According to a preferred embodiment of the present invention, impregnation is provided according to Table 1 for treating non-colored crust after the last processing bath. It is preferable that the graphene particles are added in the last bath or tumbling operation so as to avoid that subsequent tumbling may detach or separate graphene particles from the substrate.

10

% by weight of crust leather	Steps
500%	Drum + Water 40°C – 40 min
	Drain
500%	Drum + tap water – 10 min
	Drain
210%	Tap water
18%	Graphene platelet compound + drum 1440 min
	heat 55°C
	drum 360 min
20%	Ethylene-vinyl acetate (EVA) copolymer with a solid content of 53% + drum 180 min
2%	Formic acid (solution 1:10) + drum 20 min
4%	Formic acid (solution 1:10) + drum 80 min
	Cool and wash

Table 1

Graphene platelet compound of Table 1 is a mixture of water and 16% of graphene platelets, approximately yielding a 3% dry weight of graphene platelets over the weight of leather material to be treated in the tumbling bath. Other
 15 experiments provided that the maximum amount of graphene particles that can

be embedded in the leather material is 6% dry weight.

Alternatives to formic acid are acetic acid, lactic acid, phosphoric acid and other similar acids.

Preferably, crust is split crust in order to favor inclusion of graphene
5 particles.

Furthermore, temperatures higher than 50° tend to favor absorption / embedding of graphene.

In particular, graphene particles are, according to a preferred embodiment, graphene platelets or fibers having the largest dimension, for at least 90% of the
10 platelets, not greater than 8 micrometers, preferably not greater than 5 micrometers, even more preferably not greater than 3 micrometers. Preferably the particles are in the shape of flakes with lateral dimension below 8 micrometers and thickness below 40.0 nanometers, preferably below 4.0 nanometers, with an apparent density of about 40 ± 10 g/L.

Preferably, the nano-scaled graphene platelets according to the present
15 invention are in the form of one or more graphene sheets, possibly functionalized or chemically modified, wherein each sheet prevalently consists of a hexagonal lattice in 2D of carbon atoms.

Treated leather according to table 1 is then dried, e.g. at 70°C for 4 hours,
20 and provided in crust form, so as to be ready for the finishing phase.

A comparative test measuring temperature decay with a non-treated crust was carried out as follows. A non-treated crust is obtained by the same batch of non-colored crust from which the sample successively treated according to Table 1 is selected.

The heat source is an infrared axially symmetric lamp, e.g. a 230-250 V
25 Philips incandescent lamp, located at 10 centimeters above the geometric center

of a crust sample (circular test piece with a diameter of 38 mm, area 11.34 cm².) stuck on an aluminum plate of the same size, which is in turn placed on a large steel plate. In particular, the steel plate is much larger than the specimen, e.g. is a squared plate having a diagonal more than 15 times larger than the test sample,
5 in order to effectively dissipate heat generated by the lamp and not absorbed by the test sample.

Temperature sensor is e.g. a thermal camera having a distance of 8 centimeters from the sample and an inclination of about 20° with respect to an axis of the lamp, which is parallel to a substantially vertical direction.

10 During cool down, dynamically detected parameters, preferably via an acquisition software, is a mean value temperature within a sample circular area of 3.8 centimeters centered onto the lamp axis. Mean value is e.g. the mean of temperature values detected in three equidistant and axially symmetric points within the circular area.

15 The sample, having a circular shape and 3.8 centimeter diameter, is heated up to 80°C uniformly within the circular area. This is for example checked by an operator on the screen of a computer via a false color image of the test sample having a legend of color vs. temperature value.

20 Subsequently, the lamp is switched off on the acquisition over a sampling time span of 100 seconds starts when 70°C are dynamically detected by the acquisition software.

The test is carried out at room temperature, i.e. 25°C.

25 Comparison is shown in figure 1, where solid line refers to a treated leather, in particular a non-colored crust, according to the invention and dashed line refers to a standard leather, i.e. without impregnation with graphene fibers and/or particles. A decay in the temperature of more than 35% of the treated

sample is obtained in less than 20 seconds. Such decay is represented by the steeper solid curve that shows an increased ability of the leather according to the invention to dissipate heat in order to cool down faster than the comparison leather sample. The cooling down speed helps also in a condition where a
5 product lined with the treated leather, i.e. a steering wheel or a passenger seat, has a portion exposed to a heat source, e.g. sunlight because it is facing the windscreen, and another portion in shadow, e.g. the bottom portion facing the mat adjacent to the accelerator and the brake pedal.

According to a further embodiment of the present invention, during
10 finishing a further layer can be applied on the leather comprising electrically and thermally conducting particles and/or fibers in order to enhance the superficial electric conduction. This provides significant advantages in hybrid or combined applications where thermal decay matters combine with an electric conduction performance including e.g. application of sensors or the like on the finished
15 leather.

Finishing may be provided according to many techniques including spraying, releasing from a release sheet, rolling on crust or the like and particles of graphene are compatibles with all of such techniques. Indeed, particles are added to other traditional finishing additive, including an adhesive which is
20 layered, as will be explained below, when a release sheet is used or is mixed with other additives in spraying or rolling. The adhesive provides suitable adhesion of other finishing additives to the crust substrate. Whenever the adhesive is layered, it is possible that graphene is also mixed with the adhesive to provide an electrical contact between the finishing layer and the graphene treated crust
25 substrate.

A suitable amount of graphene particles in the adhesive is 26 % dry wt/dry

wt of the adhesive coating. Values higher than 30% of graphene particles / dry weight of any finishing or adhesive layer increases viscosity of the wet composition and this negatively impacts processes such as spraying and paper application. Furthermore, the finishing or adhesive layer tends to become more brittle.

In case of spray finishing one or more conventional fluidizing agents can be used to obtain the most suitable viscosity.

According to a specific non limiting example, the finishing layer is applied to the sample via releasing from a release sheet, e.g. of paper. Preferably, the finishing layer is applied on the paper sheet reaching a 3.6 gram/meter² dry weight surface density, e.g. by roller application. The paper sheet is heated to 70°C for a few minutes, for suitable evaporation of solvents. Subsequently, e.g. by roller application, the adhesive layer is applied to the dried finishing layer at a 23.5 gram/meter² dry weight surface density [corresponding to 55 g/m² of the liquid finishing compound as it is] and, afterwards, the crust is applied and lightly pressed on the adhesive layer. The resulting multilayer material is heated to 70°C for a few minutes and, finally, the paper sheet is peeled off and preferably re-used.

In order to have a comparative example the same steps in above have been duplicated by using a finishing layer without electrically conductive material.

Preferably, the finishing layer comprises particles and/or fibers of graphene and, more preferably, an adhesive layer. If the adhesive is present, also the adhesive advantageously comprises particles and/or fibers of an electrically conductive material, in particular graphene. This ensures that there is electric conductivity between the finishing layer and the graphene-impregnated crust.

According to an embodiment of electrically conducting finishing layer, the

dry weight composition is according to Table 2:

Product	Description	(%) dry wt
Larithane BTH231 by Novotex	Aliphatic polyurethane	54
GRF	Graphene platelets	26
Isolac Black LT by Samia	Carbon Black pigment	20

Table 2

Preferably, the dry weight composition is provided with suitable solvents,
 5 e.g. a polyether based solvent for the polyurethane and a further mix of iso-
 butanol, toluene and ethyl acetate, preferably in 45/45/10 volumetric
 proportion. Graphene platelets are preferably the same already described above
 for impregnation of crust leather.

According to an embodiment, an adhesive for the finishing layer preferably
 10 comprises particles and/or fibers of graphene to provide electrical conduction.
 The dry composition of one of such embodiments is according to Table 3:

Product	Description	(%) wt
RU 4049 by Stahl	Water based aliphatic polyurethane	70.5
X100/4 by Ikem	Cross-linking agent	3.4
S10 by Ikem	Anionic levelling agent	0.1
GRF	Graphene platelets	26.0

Table 3

15

Preferably, the dry weight composition is provided with suitable solvents,
 e.g. water for the polyurethane. Graphene platelets are preferably the same
 already described above for impregnation of crust.

Graphene particles and/or fibers and/or platelets in the finishing layer and
 20 the adhesive layer may or may not be identical to those used for impregnation of
 the crust.

Comparative tests to measure surface electrical conductivity are carried out considering the following standard finished leather.

Table 4 relates to a standard finishing layer:

Product	Description	(%) dry wt
Larithane BTH231 by novotex	Aliphatic polyurethane	79.6
Isolac Black LT by Samia	Carbon Black pigment	23.1

5 Table 4

Preferably, the dry composition is provided with suitable solvents, e.g. a polyether based solvent for the polyurethane and a further mix of iso-butanol, toluene and ethyl acetate, preferably in 45/45/10 volumetric proportion.

10 Table 5 relates to a standard adhesive for the above described finishing layer (dry weight):

Product	Description	(%) dry wt
RU 4049 by Stahl	Water based aliphatic polyurethane	95.2%
DF 2459 by Stahl	Anti-foam e.g. mineral oil	4.7%
Livelling ag. S10 by Ikem	Anionic levelling agent	0.1%

Table 5

15

Preferably, the dry weight composition is provided with suitable solvents, e.g. tap water for the aliphatic polyurethane and anionic components.

The finishing layer is applied to both samples via releasing from a release sheet, e.g. of paper. Preferably, both finishing layers are applied on the paper sheet reaching an overall 3,6 g/m² dry weight surface density each, e.g. by roller application and equivalent to 13 g/m² of finishing fluid mix as it is. The paper sheet is heated to 70° C for a few minutes, for suitable evaporation of

20

solvents. Subsequently, e.g. by roller application, the adhesive layer is applied to the dried finishing layer at a 23.5 gram/meter² dry weight surface density and, afterwards, the crust is applied and lightly pressed on the adhesive layer. The resulting multilayer comprising a crust substrate, an adhesive layer and a finishing layer is heated to 70° C for a few minutes and, finally, the paper sheet is peeled off and preferably re-used.

The non-treated comparative samples meet as well quality standards of the automotive and the fashion industry, e.g. for production of shoes and clothes, as the treated leather described above.

Comparative results are listed in Table 6:

Description	Graphene doping			Resistivity
	Crust	Adh. layer	Finish. layer	
Non-finished standard crust	NO	absent layer	absent layer	>1MΩ ·cm
Standard finished leather	NO	NO	NO	>1MΩ ·cm
Non-finished treated crust	YES	absent layer	absent layer	12300 Ω ·cm
Fully treated finished leather	YES	YES	YES	670 Ω ·cm

Table 6

Resistivity is measured applying two electric plate conductors, e.g. 1 centimeter squared conductors, distanced by 1 centimeter on the surface of the non-finished crust and finished leather, whichever is applicable. Electrodes of a tester are applied to the plate conductors to measure resistivity.

The mere impregnation of crust with graphene particles and/or fibers significantly lowers electric resistivity; additional graphene particles and/or fibers in the finishing layer and the adhesive provide an even more enhanced conductivity, i.e. a much lower resistivity.

5 The leather treated according to the invention can be applied as an external layer or lining for many friction-wearable elements, e.g. steering wheel, seats, front and rear door internal handles and the like. It preserves a soft touch surface over the working life of the vehicle and, in the particular case of seats, a relatively high elasticity and softness and reduces or avoids cracks after a number of
10 deformations due to seating of the user.

Moreover the leather treated according to the invention can be used to produce wearable products such as shoes, watch straps, dresses; or in accessories such as backpacks, purses and other leather goods such as a cover for smartphone or the like, safety footwear to be used in environments where there are heat
15 sources, or protective clothings that are worn even under strong solar radiation, such as biker suits or firemen's clothing.

CLAIMS

1. A thermally conductive modified natural or synthetic leather material adapted for a lining of a product, in particular for the passenger compartment of a vehicle, comprising a thermally conductive agent including graphene particles;

5 Wherein

- the material comprises a crust substrate impregnated with the thermally conductive agent at a sufficient concentration to provide thermal conductivity in the modified material;

10 - the material further comprises one or more layers applied on the substrate and comprising graphene particles; and

the modified material having a thermal decay of 29% or more starting from 70°C at ambient temperature of 21°C in less than 20 seconds.

15 2. The thermally conductive modified material according to claim 1, wherein the graphene particles comprise platelets and/or fibers and corresponding mixtures.

3. The thermally conductive modified material according to anyone of claims 1-2, wherein the substrate is split crust.

20 4. The thermally conductive modified material according to anyone of claims 1-3, wherein the one or more layers are such that there is electric conductivity with the substrate and electric resistivity is lower than 10000 Ohm*cm.

25 5. The thermally conductive modified material according to claim 4, wherein the one or more layers comprise no more than 30% of graphene particles in dry weight of each layer composition and/or no more than a 10 grams/m² of graphene particles as an overall surface density within the one or more layers as a whole.

6. The thermally conductive modified material according to any of the preceding claims, wherein a first surface density (grams/m²) of graphene particles in the adhesive layer is greater than a second surface density of graphene particles in the finishing layer.

5 7. The thermally conductive modified material according to any of the preceding claims, wherein the thermal decay is of 35% or more starting from 70°C at ambient temperature of 21°C in less than 20 seconds.

8. A method to modify a natural or synthetic leather material for providing a thermal conductivity in the modified material, said method comprising the step
10 of:

- impregnating a crust substrate with an aqueous bath comprising no more than 6% dry weight of graphene particles with respect to the substrate as a thermally conductive agent;

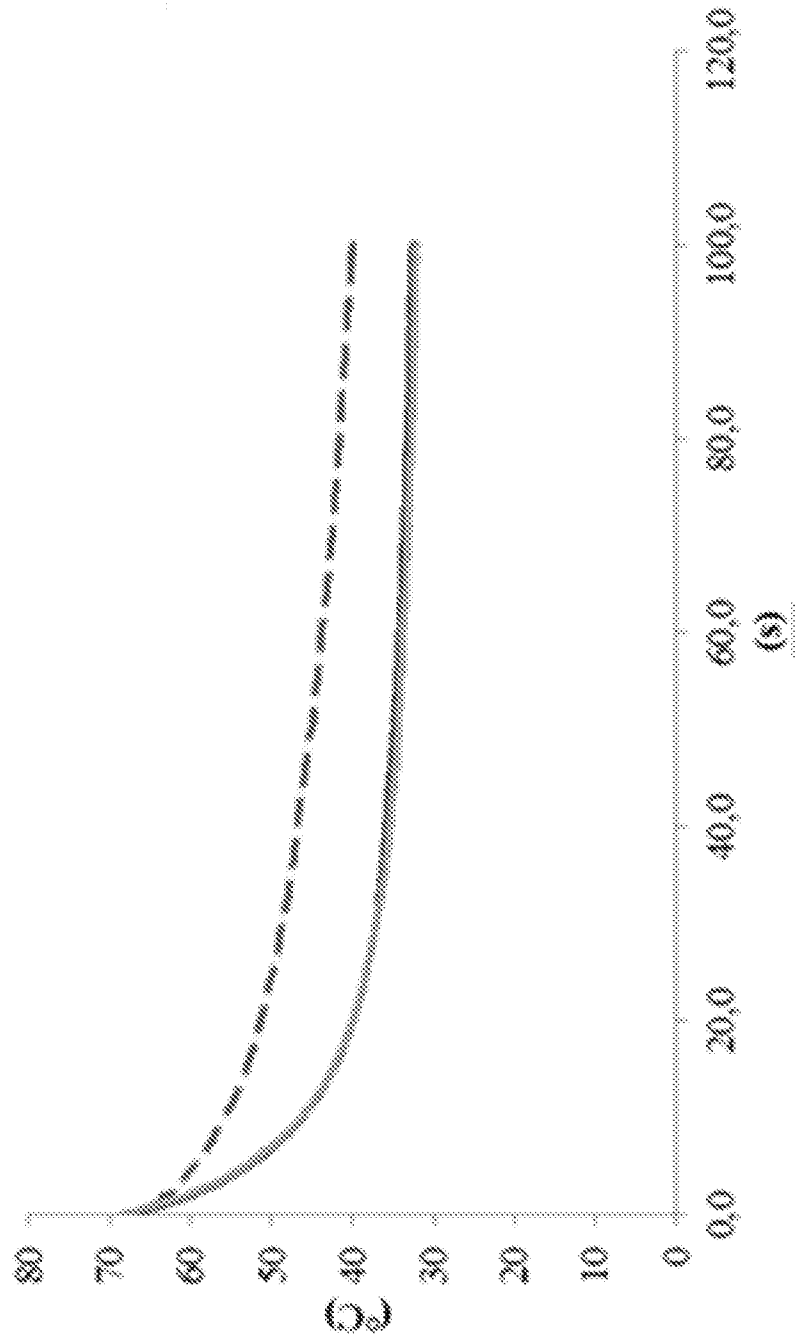
- applying on the substrate one or more layers comprising graphene
15 particles.

9. The method according to claim 8, wherein the graphene particles are between 2,5 and 5% dry weight with respect to the substrate.

10. The method according to one of claims 8 or 9, wherein the graphene particles for impregnation are added to the last tumbling bath of the substrate.

20

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/058819

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C01B32/182 C14B1/00 D06N3/00 B32B9/02 C14B7/02
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 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C01B D06Q C14B D06N H05B B32B H01B
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/376832 A1 (LI LI [HK] ET AL) 31 December 2015 (2015-12-31) abstract paragraphs [0003], [0063], [0067], [0069], [0073], [0083] claims 1-20	1-10
Y	US 2017/282767 A1 (KOZLOWSKI ERIC [US]) 5 October 2017 (2017-10-05) abstract figure 3 paragraphs [0008], [0012], [0016], [0018] claims 1-6	1-10
Y	CN 106 675 006 A (HUAFON MICROFIBRE CO LTD) 17 May 2017 (2017-05-17) abstract	1-10
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Further documents are listed in the continuation of Box C. See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

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