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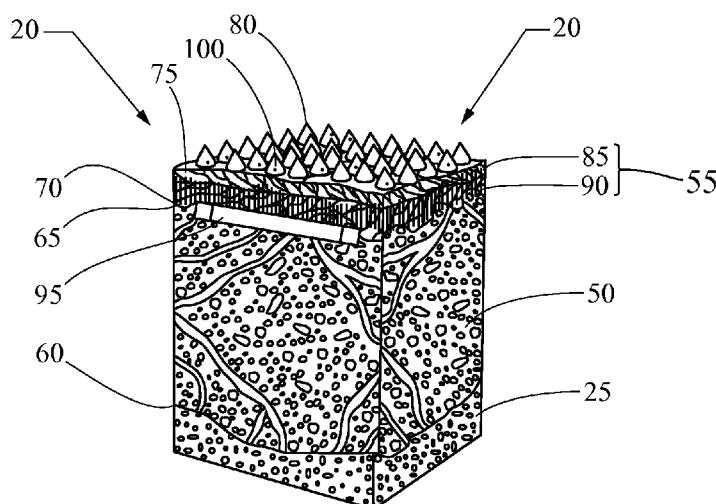


Fig. 3B

(57) Abstract: An external covering (20) and method of making an external covering for hiding the internal endoskeleton of a mechanical (e.g., prosthetic) device that exhibits skin-like qualities is provided. The external covering generally comprises an internal bulk layer (50) in contact with the endoskeleton of the prosthetic device and an external skin layer (55) disposed about the internal bulk layer. The external skin layer is comprised of a polymer composite (85) with carbon nanotubes (90) embedded therein. The outer surface (75) of the skin layer has multiple cone-shaped projections (80) that provide the external skin layer with superhydrophobicity. The carbon nanotubes are preferably vertically aligned between the inner surface and outer surface of the external skin layer in order to provide the skin layer with the ability to transmit heat. Superhydrophobic powders may optionally be used as part of the polymer composite or applied as a coating to the surface of the skin layer to enhance superhydrophobicity.

## **SELF-CLEANING SKIN-LIKE PROSTHETIC POLYMER SURFACES**

### **FIELD**

**[0001]** This invention relates generally to the field of prosthetics. More specifically, this invention pertains to the use of nanotechnology to create tough, self-cleaning polymer surfaces that simulate skin-like properties for use as a covering for a prosthetic device.

### **BACKGROUND**

**[0002]** Artificial arms and legs, as well as other prostheses attempt to restore normal function to amputees. Part of this normal function is the physical or aesthetic appearance of the prosthetic limb. One major problem with existing prosthetic devices is that their exterior surface does not exhibit many of the characteristics of human skin, such as toughness, flexibility, heat and pressure sensation, water repellency, and smoothness. The lack of toughness and flexibility in existing prostheses causes the exterior surface of these prostheses to wrinkle or become distorted when they are stretched or compressed. In addition, the polymers currently used in making the prosthetic covering, generally behave as a thermal insulator, thereby preventing the quick detection and transmittal of thermal readings to embedded heat sensors. This time lapse often creates a problem by allowing the polymer to begin melting before the embedded thermal sensor can detect a change in temperature.

**[0003]** Accordingly, while significant advances have been made in the prosthetic industry over the past decade, there exists a continual desire to provide prostheses with enhanced performance and aesthetic appeal. In particular, a prosthetic device having an exterior surface that exhibits the characteristics of real human skin is highly desirable.

### **SUMMARY**

**[0004]** The present disclosure provides an external covering for hiding the internal endoskeleton of a mechanical device (e.g., prosthetic device) that provides skin-like qualities. One embodiment of an external covering constructed in accordance with the teachings of the present disclosure, generally comprises an

internal bulk layer in contact with the endoskeleton of the mechanical device and an external skin layer disposed about the internal bulk layer. The external skin layer is comprised of a polymer composite with carbon nanotubes embedded therein. The outer surface of the skin layer has multiple cone-shaped projections that provide the external skin layer with superhydrophobicity. The carbon nanotubes are preferably vertically aligned between the inner surface and outer surface of the external skin layer in order to provide the skin layer with enhanced thermal conductivity, i.e., the ability to transmit heat. The mechanical properties exhibited by the external skin layer may be enhanced by selecting the orientation or alignment angle for the carbon nanotubes in the skin layer. The mechanical properties may further be enhanced by exposing the carbon nanotubes to a high temperature annealing procedure. According to another aspect of the present disclosure, a superhydrophobic powder may optionally be used as part of the skin layer or applied as a coating to the surface of the skin layer to enhance superhydrophobicity of the skin layer.

**[0005]** Another embodiment of the present disclosure provides a method of making the external covering described above for use with a mechanical device whose surface exhibits skin-like qualities. This method generally comprises providing a mold having a cavity with a predetermined shape and at least one surface having a nano-funnel or micro-funnel patterned array. A film comprised of a polymer composite with embedded carbon nanotubes is inserted into the cavity of the mold and allowed to contact the patterned surface of the mold's cavity. Then heat, vacuum, pressure, or a combination thereof is applied to the cavity and/or the film to cause the film to conform to the predetermined shape of the mold and to induce the formation of superhydrophobic cone-shaped projections on the surface of the film. After the shaped film is cooled and removed from the mold, it is adhered to a pre-shaped internal bulk layer to form the external covering.

**[0006]** According to another aspect of the present disclosure the step in which the shaped film is adhered to the pre-shaped internal bulk layer may be replaced with the step of back-molding the internal back layer to be in contact with the film. According to yet another aspect of the present disclosure, the method may further comprise the step of opening a gap in the mold and injecting an in-mold coating into the gap to coat the surface of the film.

**[0007]** Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0008]** The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way.

**[0009]** Figure 1A is a perspective view of an endoskeleton for a transtibial prosthetic device;

**[0010]** Figure 1B is a perspective view of a prosthetic device made according to the teachings of the present disclosure that includes the endoskeleton of Figure 1A;

**[0011]** Figure 2A is a perspective view of an endoskeleton for a transhumeral prosthetic device;

**[0012]** Figure 2B is a perspective view of a prosthetic device made according to the teachings of the present disclosure that includes the endoskeleton of Figure 2A;

**[0013]** Figure 3A is a cross-sectional view of human skin highlighting the dermis and epidermis layers;

**[0014]** Figure 3B is a cross-sectional view of an external covering made according to the teachings of the present disclosure;

**[0015]** Figure 4A is a cross-sectional micrograph image of the external skin layer associated with the external covering of Figure 3B.

**[0016]** Figure 4B is a cross-sectional schematic representation of an external skin layer prepared according to one aspect of the present disclosure highlighting both hard and soft segments;

**[0017]** Figure 4C is a cross-sectional schematic representation of an external skin layer highlighting possible differences in orientation for the carbon nanotubes in the polymer composite according to one aspect of the present invention;

**[0018]** Figure 5A is a graphical representation of the enhancement obtained in the mechanical properties of the external skin layer plotted as a function of carbon nanotube orientation;

**[0019]** Figure 5B is a graphical representation of the enhancement obtained in the mechanical properties of the external skin layer plotted as a function of carbon nanotube orientation after the nanotubes are exposed to a high temperature, annealing procedure;

**[0020]** Figure 5C is a graphical representation of the scratch resistance obtained for the external skin layer at various carbon nanotube orientations depicted as the amount of penetration plotted as a function of scratch distance;

**[0021]** Figure 6A is a flowchart of a manufacturing process for an exterior covering for use in a mechanical (e.g., prosthetic) device according to one embodiment of the present disclosure;

**[0022]** Figure 6B is a flowchart of a manufacturing process for an exterior covering for use in a mechanical (e.g., prosthetic) device according to another aspect of the present disclosure; and

**[0023]** Figure 6C is a flowchart of a manufacturing process for an exterior covering for use in a mechanical (e.g., prosthetic) device according to yet another aspect of the present disclosure.

## DETAILED DESCRIPTION

**[0024]** The following description is merely exemplary in nature and is in no way intended to limit the present disclosure or its application or uses. It should be understood that throughout the description and drawings, corresponding reference numerals indicate like or corresponding parts and features.

**[0025]** The present disclosure generally provides an external covering for a mechanical device, such as a prosthetic device, used as a replacement for a human limb that requires the outer layer of the prosthesis to have a skin-like exterior surface. As shown in Figures 1(A-B) and 2(A-B), examples of such prostheses 5 include, but are not limited to, those used as transtibial, transfemoral, transradial, or transhumeral replacements for human limbs. By definition, transtibial and transfemoral prostheses replace legs that are missing from below the knee and from above the knee, respectively. Likewise, transradial and

transhumeral prostheses replace arms missing from below the elbow and from above the elbow, respectively. In Figures 1(A-B) and 2(A-B) the prostheses shown are transfemoral and transhumeral prostheses, respectively. One skilled-in-the-art will understand that the external covering 20 for a prosthesis as described in this disclosure may be incorporated with any type of prosthesis 5 used as a replacement for a human limb that requires a skin-like exterior surface. One skilled-in-the-art will further understand that the external covering of the present disclosure may be used with the endoskeleton or internal support structure associated with other types of mechanical devices or equipment without departing from scope of the invention.

**[0026]** The prosthetic device 5 is comprised of an internal endoskeleton 25 or pylon structure that may include joints 30, as well as a means (e.g., belts, cuffs, etc.) to attach the prosthesis to the human body. The internal endoskeleton 25 is then covered with an external covering 20 to provide physical protection for the endoskeleton 25 and to aesthetically provide a skin-like appearance. The prosthesis may be integrated with the functioning of the human body through the use of various biosensors, signal controllers, and actuators. The endoskeleton 25 may be made from any light weight material, such as plastics, metals, or alloys. Examples of such light weight materials include polypropylene, titanium, aluminum, and carbon fiber composites.

**[0027]** The external covering 20 is designed and adapted to resemble the appearance and performance of human skin. As shown in Figure 3A, real human skin 35 is generally comprised of an inner bulk layer called the dermis layer 40 and an outer thin layer called the epidermis layer 45. The dermis layer 40 is in contact with subcutaneous tissue 41 of the human body. The epidermis layer 45 contains a melanin pigment that helps to counteract the absorption of the light rays from the sun by darkening the color of the skin 35.

**[0028]** Similar to human skin 35, the external covering 20 of the current disclosure is comprised of multiple layers as shown in Figure 3B. Primarily, the external covering 20 comprises an internal bulk layer 50 and an external skin layer 55. The internal bulk layer 50 has a first side 60 and second side 65 with the first side 60 being in contact with the internal endoskeleton 25 of the prosthetic device 5. The external skin layer 55 is disposed about the second side 65 of the internal

bulk layer 50. The external skin layer 55 has an inner surface 70 and an outer surface 75. The inner surface 70 being in contact with the second side 65 of the bulk layer 50 and the outer surface 75 representing the external surface of the prosthetic device 5.

**[0029]** The outer surface 75 of the external skin layer 55 exhibits a nano-cone or micro-cone pattern 80, projections, or structure. The external skin layer 55 is further comprised of a polymer composite 85 and an embedded network of carbon nanotubes 90. The carbon nanotubes 90 are preferably vertically aligned or in other words, positioned to be about perpendicular to the outer surface 75 as shown in Figure 4A. The carbon nanotubes 90 may occupy from about 1% to about 40% of the volume associated with the external skin layer 55.

**[0030]** The nano-cone or micro-cone 80 pattern represents nanometer or micrometer size surface irregularities predetermined to be located on the outer surface 75 of the prosthetic device 5. These nano-cone or micro-cone 80 irregularities may be protrusions or projections arising out of the outer surface 75 of the external skin layer 55. These irregularities or projections, which are formed as an integral part of the external skin layer 55, may vary the height, spacing, shape, and characteristics of this layer's outer surface 75.

**[0031]** Embedding carbon nanotubes 90 into the external skin layer 55 of the prosthesis 5 provides for enhanced features, such as toughness, strength, and durability. In fact, the external skin layer 55 is designed to be tougher and stronger than the internal bulk layer 50. The carbon nanotubes 90 exhibit high tensile strength and elastic modulus in the axial direction, while being relatively soft in the radial direction. Thus the external skin layer 55 may exhibit a tough outer surface 75, while maintaining a relatively high degree of flexibility.

**[0032]** The external skin layer 55 may be constructed to exhibit a gradient in mechanical properties by controlling the orientation or alignment of the carbon nanotubes 90, as well as the spacing between the nanotubes 90 embedded in the polymer composite 85 of the skin layer 55. Referring to Figure 4B, the external skin layer 55 may comprise multiple layers of embedded nanotubes 90 and layers of polymer composite 85 that are absent of any nanotubes 90. When the nanotubes 90 are vertically aligned with the outer surface 75 of the external skin layer 55 they represent a tough, hard segment or layer 91. In comparison, the

polymer composite 85 absent any nanotubes 90 represents a relatively soft segment or layer 86. In other words, the mechanical properties exhibited by a layer of the polymer composite 85 with embedded nanotubes 90 is enhanced over the pure polymer properties of the composite 85 layer. Embedding carbon nanotubes 90 into the polymer composite 85 provides for anisotropic enhancement of the mechanical properties exhibited by the external skin layer 55. The extent of this enhancement depends upon the directional alignment of the nanotubes 90, the structure or type of nanotubes 90, the amount or loading of nanotubes 90 in the external skin layer 55, and the composition of the polymer composite 85, among other factors. In fact, the extent of this enhancement may be larger when a relatively "soft" polymer composite 85 is used and smaller when a relatively "hard" polymer composite 85 is used.

**[0033]** When the carbon nanotubes 90 are vertically aligned with the outer surface 75 of the external skin layer 55, they are orientated in a direction that is parallel to the applied load 93, thereby, providing for a large enhancement in mechanical properties. As shown in Figure 4C, a layer 89 in which the embedded carbon nanotubes 90 are perpendicular ( $90^\circ$ ) to the mechanical load 93 will not be as "hard" as a layer 91 where the nanotubes 90 are parallel ( $0^\circ$ ) to the mechanical load 93 and not as "soft" as a layer 86 comprised of the pure polymer composite 85. Carbon nanotubes 90 that are perpendicular to the mechanical load 93 are aligned to be parallel with the outer surface 75 of the external skin layer 55. An intermediate enhancement in mechanical properties may result when the layer 92 has nanotubes 90 oriented in a direction that is between the vertical ( $0^\circ$ ) alignment of layer 91 and the perpendicular ( $90^\circ$ ) alignment of layer 89. In Figure 4C, the intermediate layer 92 is shown with nanotubes 90 aligned at a  $45^\circ$  angle to the mechanical load 93. One skilled-in-the-art will understand that the carbon nanotubes 90 may be aligned or oriented with respect to the mechanical load 93 at any angle between  $0^\circ$  and  $90^\circ$ .

**[0034]** For example, the mechanical properties exhibited by an external skin layer 55 comprising about 10 wt. % multi-walled carbon nanotubes 90 in an epoxy polymer composite 85 were measured at about  $25^\circ\text{C}$  using a nanoindenter equipped with a Berkovich tip. A summary of the enhancement in mechanical properties observed for the external skin layer 55 upon incorporation of carbon

nanotubes 90 into the polymer composite 85 is plotted in Figure 5A as a function of nanotube 90 alignment with respect to the direction of the applied load 93. The origin point 105 of the plot (e.g., 0% enhancement) represents the mechanical properties exhibited by the pure polymer composite 85 without the incorporation of any carbon nanotubes 90. Upon the incorporation of nanotubes 90 into the polymer composite 85 an enhancement in mechanical properties, such as Young's modulus 110, hardness 111, polymer creep 112, and scratch resistance 120, is observed. An enhancement in polymer creep may be defined as a reduction in the permanent deformation of the polymer that occurs when the polymer composite 85 is exposed to a constant applied stress.

**[0035]** Referring to Figure 5A, the maximum enhancement in Young's modulus 110 of 40% occurs when the carbon nanotubes 90 are aligned parallel with the applied load 93. The hardness of the external skin layer 55 can be increased between about 17% to about 25% compared to the pure polymer composite 85 upon the incorporation of nanotubes 90 into the polymer composite 85 with the largest enhancement occurring when the nanotubes 90 are aligned perpendicular to the load 93. Similarly, the largest enhancement with respect to reducing polymer deformation or creep 112 is provided when the embedded carbon nanotubes 90 are aligned perpendicular to the applied load 93.

**[0036]** An optional high temperature annealing procedure that exposes the carbon nanotubes 90 to a temperature up to about 2,400°C can be used to further enhance the mechanical properties exhibited by the external skin layer 55. It is possible that exposure of the nanotubes 90 to this annealing procedure reduces the existence of surface/wall defects in the nanotubes 90, which in turn increases the crystallinity and overall stiffness of the nanotubes 90. Thus this annealing procedure can be used to enhance the mechanical properties exhibited by the external skin layer 55 with having to alter the orientation of the nanotubes 90 in the layer 55.

**[0037]** Referring now to Figure 5B, after annealing the carbon nanotubes an enhancement of about 71% in Young's modulus 110 is observed when about 10 wt. % of the carbon nanotubes 90 are embedded in the polymer composite 85 and are aligned parallel to the applied load 93. The hardness of the external skin layer 55 with embedded carbon nanotubes can be increased up to about 34% over the

pure polymer composite 85, and polymer deformation or creep 112 can be reduced by about 29% when the carbon nanotubes 90 are annealed and then aligned perpendicular to the applied load 93.

**[0038]** The overall range of enhancement for Young's modulus 110, hardness 111, and polymer creep 112 attributable to annealing the carbon nanotubes 90, aligning the nanotubes 90 in the polymer composite 85, or a combination of both is between about 22 to 80%, about 13 to 34%, and about 13 to 29%, respectively, when about 10 wt.% nanotubes 90 are incorporated into the polymer composite 85 of the external skin layer 55. Further enhancement of the mechanical properties can occur upon the incorporation of a greater weight percentage of carbon nanotubes 90 into the polymer composite 85. The incorporation of about 40 wt. % carbon nanotubes 90 into the polymer composite 85 may increase Young's modulus 110, increase hardness 111, and reduce polymer creep 112 by as much as about 320%, 134%, and 116%, respectively.

**[0039]** Referring now to Figure 5C, the effect of the alignment or orientation of carbon nanotubes in the external skin layer 55 on improving the scratch resistance 120 exhibited by the skin layer is shown. Carbon nanotubes 90 oriented perpendicular 125 to the scratch direction in an epoxy polymer composite 85 provide about a 90% reduction in surface penetration when compared to the pure polymer composite 85. When the carbon nanotubes 90 are oriented parallel 130 to the scratch direction, the reduction of surface penetration is about 58%. One skilled-in-the-art will understand that although the scratch conditions utilized were 0.1mN load over 100 mm distance at 0.5 mm/s, similar results would be obtained using a different set of standard conditions. The scratch resistance can be further tuned by controlling the type of nanotube (e.g., single nanotube, few wall nanotubes, or double wall nanotubes), as well as controlling the weight loading, the incorporation of other additives (i.e., metal oxide structures) on the surface or between nanotubes.

**[0040]** The external skin layer 55 with embedded carbon nanotubes 90 can also conduct heat and provide for pressure sensation. The presence of the carbon nanotubes 90 enhances the ability of the outer surface 75 to conduct electrical current and heat. Thus a variety of different sensors 95 may be optionally located in the internal bulk layer 50 that can detect temperature or pressure changes

occurring in the external skin layer 55, thereby, imitating the performance of real skin nerve cells.

**[0041]** The nano-cone or micro-cone 80 patterns provide the outer surface 75 of the external skin layer 55 with superhydrophobicity, thereby, keeping the external surface of the prosthesis clean and dry. The superhydrophobicity of the outer surface 75 is preferably described as the surface having a contact angle greater than about 150 degrees when a drop of water is applied to the surface.

**[0042]** Referring to Figure 3B, superhydrophobic powders 100 may optionally be incorporated into or onto the outer surface 75 of the external skin layer 55, thereby providing an additional mechanism through which water may be repelled. Preferably, the superhydrophobic powders 100 comprise at least one hydrophobic material selected as one from the group of perfluorinated organics, fluorinated organics, and self-assembled monolayers. Other examples of superhydrophobic powders include those described in co-pending U.S. patent application No. 11/837,076 filed August 10, 2007, herein incorporated by reference.

**[0043]** Carbon nanotubes 90 exhibit a range of different colors depending on their size, shape, and length. The carbon nanotubes 90 may be sorted and selected by size to provide a predetermined color to the external skin layer 55. Thus the external skin layer 55 may be designed to match the color associated with the rest of a person's skin 35, thereby, making the external surface of the prosthesis appear much more skin-like and natural.

**[0044]** The carbon nanotubes 90 as embedded in or applied to the external skin layer 55 may be single-wall (SWNTs) or multiwall (MWNTs) structures exhibiting either metallic conducting or semiconducting behavior. Carbon nanotubes are allotropes of carbon having a nanostructure with a large length to diameter ratio. Preferably, the diameter of the nanotubes is on the order of a few nanometers with a length up to several millimeters. Preferably, the carbon nanotubes are vertically aligned or, in other words, perpendicular to the outer surface 75 of the external skin layer 55 in order to enhance the desired affects. The nanotubes are embedded in a polymer composite 85 or in an applied surface coating in a manner that stabilizes the architecture of the nanotubes 90 in the predetermined vertical alignment, direction, or pattern.

**[0045]** The carbon nanotubes 90 can be grown from or deposited by plasma enhanced chemical vapor deposition (PECVD) or any other method known to one skilled-in-the-art, including but not limited to chemical vapor deposition, arc discharge, laser ablation, high pressure carbon monoxide (HiPCO), spray coating, dip coating, and flow coating.

**[0046]** The polymer composite 85 of the exterior skin layer 55 or optionally a coating applied to the outer surface 75 of the exterior skin layer 55 may be made of any known thermoplastic or elastomeric material, such as polyimides, fluoropolymers, polyamides, polyesters, silicones, polyurethanes, epoxies, or polyacrylates, among others. Preferably, the polymer composite or coating is comprised of a polyimide material.

**[0047]** The interior bulk layer 50 may be comprised of any fabric, foam, silicone, gelatin, latex, collagen, sponge, wool, cotton, or a mixture or combination thereof. One skilled-in-the-art will understand that the interior bulk layer 50 may be comprised of any other material that will provide for the physical protection of the underlying endoskeleton 25 without departing from the scope of this disclosure.

**[0048]** The exterior skin layer 55 may be fastened to the underlying interior bulk layer 50 and the interior bulk layer 50 may be fastened to the underlying endoskeleton 25 by any means known to one skilled-in-the-art. Such means includes, but is not limited to, the use of adhesives, coupling agents, mechanical fasteners, and melt bonding.

**[0049]** It is another objective of the present disclosure to provide a method 199 of making or manufacturing an exterior covering 20 for use with an endoskeleton 25 to form a mechanical device, such as a prosthetic device 5. One aspect of the present disclosure is to provide a method of forming a prosthesis 5 that includes the previously described exterior covering 20. Referring to Figure 4A, a method of forming an external covering 20 for use with a mechanical (e.g., prosthetic) device generally comprises the steps of providing 200 a mold having a cavity with a predetermined shape. The mold includes at least one surface having a nano-funnel or micro-funnel array. A more detailed description of the nano-funnel or micro-funnel array surface of the mold as used herein is provided in co-pending U.S. patent application No. 11/945,865 filed November 27, 2007, which is hereby incorporated by reference.

**[0050]** A film, which will form the external skin layer 55, is then inserted 210 into the cavity of the mold. In such, this film is comprised of the polymer composite 85 embedded with carbon nanotubes 90. If desirable, the carbon nanotubes may be optionally subjected to an annealing 205 procedure prior to being incorporated into the film. Optionally, superhydrophobic powder 100 may be applied 215 to the surface of the film. Heat, vacuum, and/or pressure are then applied 220 to induce the formation of an external skin layer 55 exhibiting a superhydrophobic outer surface 75. The application of heat may be accomplished by heating the mold or heating the film. The surface of the film is caused to melt or deform and to take on the shape of the funnel array surface of the mold. The translation of the mold nano-funnel or micro-funnel surface onto the film results in the formation of nano-cones or micro-cones 80 on the outer surface 75 of the external skin layer 55. The external skin layer 55 is then removed 230 from the mold. One skilled-in-the-art will understand that the preceding steps 200, 210, 215, and 220 associated with forming the external skin layer 55 may be varied according to any known steps used in a thermoforming process without departing from the scope of this disclosure.

**[0051]** The external skin layer 55 is then fastened or adhered 240 to a pre-shaped internal bulk layer 50 to form the external covering 20 for use in a prosthetic device 5. Optionally, the formation of a prosthetic device 5 may be completed by fastening 250 the internal bulk layer 50 of the external covering 20 to an endoskeleton 25. One skilled-in-the art will understand that the external covering 20 may be applied to an endoskeleton 25 that represents the internal structure or support for other types of mechanical devices and is not limited to use only with prosthetic devices 5.

**[0052]** According to another aspect of the present disclosure, a method 299 resembling a film-insert molding or in-mold decorating process may be utilized. Referring now to Figure 4B, in this method 299 a mold is provided 300 having a cavity with a predetermined shape. This mold includes at least one surface having a nano-funnel or micro-funnel array as previously described.

**[0053]** A film, which will form the external skin layer 55, is then inserted 310 into the cavity of the mold. In such, this film is comprised of the polymer composite 85 embedded with carbon nanotubes 90. If desirable, the carbon nanotubes may

be optionally subjected to an annealing 305 procedure prior to being incorporated into the film. Optionally, superhydrophobic powder 100 may be included on the surface of this film. Heat, vacuum, and/or pressure may then be applied 320 to induce the formation of an external skin layer 55 exhibiting a superhydrophobic outer surface 75. The heat may be applied by heating the mold or heating the film. The surface of the film is caused to melt or deform and to take on the shape of the funnel array surface of the mold. The translation of the mold nano-funnel or micro-funnel surface onto the film results in the formation of nano-cones or micro-cones 80 on the outer surface 75 of the external skin layer 55.

**[0054]** Finally, the internal bulk layer 50 may be back-molded 330 onto the external skin layer 55 to form the external covering 20. The internal bulk layer 50 may adhere to the external skin layer 55 by melt bonding or by adhesion when the film includes an adhesive on the surface that is forced into contact with the internal bulk layer 50 during the back-molding step. The external covering 20 is then removed 340 from the mold to complete the process 299 of forming an external covering 20 for a prosthetic device 5. Optionally, the formation of the prosthetic device 5 may then be completed by fastening 350 the internal bulk layer 50 of the external covering 20 to the endoskeleton 25. One skilled-in-the-art will understand that the preceding steps 300, 310, 320, and 330 associated with forming the external skin layer 55 may be varied according to any known steps used in a film-insert molding process without departing from the scope of this disclosure.

**[0055]** According to yet another aspect of the present disclosure, a method 399 that integrates the film-insert molding method 299 with an in-mold coating delivery system may be utilized. In order to effectively apply a coating during the molding operation, a rotating stack mold with at least one needle gate to inject the coating formulation is preferably used along with a coating metering unit or delivery cart.

**[0056]** Referring now to Figure 4C, in this method 399 a mold is provided 400 that has a cavity with a predetermined shape and at least one surface having a nano-funnel or micro-funnel array as previously described. The film, which will form the external skin layer 55, is then inserted 410 into the cavity of the mold. If desirable, the carbon nanotubes may be optionally subjected to an annealing 405 procedure prior to being incorporated into the film. Heat, vacuum, and/or pressure

may then be applied 420 to induce the formation of an external skin layer 55 exhibiting a superhydrophobic outer surface 75. The internal bulk layer 50 is then back molded 430 onto the external skin layer 55 to form the external covering 20. The internal bulk layer 50 may adhere to the external skin layer 55 by melt bonding or by any other known means.

**[0057]** Finally, a very small mold gap (depending on the desired coating thickness) is then opened 440 and a measured amount of an in-mold coating (IMC) is injected into the gap. The IMC coating can be injected between the outer surface 75 of the external skin layer 55 and the surface of molding containing the nano-funnel or micro-funnel surface. The mold is then closed, clamped, coin/compressed, and the coating cured. Depending on the specific formulation of the IMC coating and the required cure conditions, additional heating or cooling of the mold may be necessary to fully cure the coating. In this way the coating will upon cure exhibit the contour of a nano-cone or micro-cone surface rather than cause the planarization of the outer surface 75. Optionally, this coating may include superhydrophobic powder 100 as a filler material. One skilled-in-the-art will understand that the preceding step of applying 440 an in-mold coating to the outer surface 75 of the external skin layer 55 may be varied according to any known steps used in an in-mold coating process without departing from the scope of this disclosure. In addition, multiple additional steps related to coining and clamping may be required. It is further understood that the in-mold coating step described above may also be incorporated into the thermoforming method described in Figure 4A.

**[0058]** Finally, the external covering 55 is cooled, the mold opened, and the covering 55 removed 450 from the mold. Optionally, the formation of the prosthetic device 5 may then be completed by fastening 460 the internal bulk layer 50 of the external covering 20 to an endoskeleton 25.

**[0059]** One skilled-in-the-art will understand that the foregoing description is not intended to limit the use of the external covering to the application of prosthetic devices. Rather the external covering of the present disclosure is equally applicable for use in other applications, such as a covering for an endoskeleton, which may include, but not be limited to, mechanical equipment, mechanical devices, or other mechanical structures, that are used in or by other industries,

such as automotive or aerospace. For example, the external covering may be applicable for use as a seat covering or an overlay for a dashboard or instrument panel to name a few.

**[0060]** The foregoing description of various embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Numerous modifications or variations are possible in light of the above teachings. The embodiments discussed were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

## CLAIMS

What is claimed is

1. An external covering 20 for hiding the internal endoskeleton 25 of a mechanical device 5 that provides skin-like qualities, the external covering 20 comprising:

an internal bulk layer 50 having a first side 60 and a second side 65 with the first side 60 being in contact with the internal endoskeleton 25 of the mechanical device 5; and

an external skin layer 55 having a higher level of toughness than the internal bulk layer 50;

wherein the external skin layer 55 is characterized by a polymer composite 85 with carbon nanotubes 90 embedded therein disposed about the second side 65 of the bulk layer 50, the skin layer 55 having an inner surface 70 and an outer surface 75; the inner surface 70 being in contact with the bulk layer 50 and the outer surface 75 having multiple cone-shaped projections 80; the cone-shaped projections 80 providing the external skin layer 55 with superhydrophobicity, while the embedded carbon nanotubes 90 provide the skin layer 55 with enhanced thermal conductivity.

2. The external covering 20 of Claim 1, wherein the cone-shaped projections 80 are selected as one from the group consisting of nanometer sized nano-cones and micrometer sized micro-cones.

3. The external covering 20 of Claim 1, wherein the size, shape, and length of the carbon nanotubes 90 are selected to provide a predetermined color shade intended to resemble a person's natural skin color.

4. The external covering 20 of Claim 1, wherein the external covering 20 further comprises at least one sensor 95 embedded in the internal bulk layer 50 that is in contact with the carbon nanotubes 90 in the external skin layer 55.

5. The external covering 20 of Claim 1, wherein the carbon nanotubes 90 occupy about 1% to about 40% of the volume associated with the external skin layer 55.

6. The external covering 20 of Claim 5, wherein the carbon nanotubes 90 are vertically aligned between the inner surface 70 and the outer surface 75 of the external skin layer 55.

7. The external covering 20 of Claim 5, wherein the carbon nanotubes 90 are oriented in the external skin layer 55 such that the external skin layer 55 exhibits a predetermined amount of enhancement in at least one mechanical property selected from the group consisting of Young's modulus, hardness, scratch resistance, and polymer creep.

8. The external covering 20 of Claim 1, wherein the outer surface 75 of the external skin layer 55 further comprises a superhydrophobic powder 100.

9. The external covering 20 of Claim 1, wherein the polymer composite 85 of the external skin layer 55 comprises at least one composition selected from the group consisting of polyimides, fluoropolymers, polyamides, polyesters, silicones, polyurethanes, epoxies, and polyacrylates.

10. A mechanical device 5 having an exterior surface that provides skin-like qualities, the mechanical device 5 comprising:

an internal endoskeleton 25; and

an external covering 20, the external covering comprising:

an internal bulk layer 50 having a first side 60 and a second side 65 with the first side 60 being in contact with the internal endoskeleton 25 of the mechanical device 5; and

an external skin layer 55;

wherein the external skin layer 55 is characterized by a polymer composite 85 with carbon nanotubes 90 embedded therein disposed about the second side 65 of the bulk layer 50, the skin layer 55 having an inner surface 70

and an outer surface 75; the inner surface 70 being in contact with the bulk layer 50 and the outer surface 75 having multiple cone-shaped projections 80; the cone-shaped projections 80 providing the external skin layer 55 with superhydrophobicity, while the embedded carbon nanotubes 90 provide the skin layer 55 with enhanced thermal conductivity.

11. The mechanical device 5 of Claim 10, wherein the cone-shaped projections 80 on the outer surface 75 of the external skin layer 55 are selected as one from the group consisting of nanometer sized nano-cones and micrometer sized micro-cones.

12. The mechanical device 5 of Claim 10, wherein the size, shape, and length of the carbon nanotubes 90 are selected to provide a predetermined color shade intended to resemble a person's natural skin color.

13. The mechanical device 5 of Claim 10, wherein the external covering 20 further comprises at least one sensor 95 embedded in the internal bulk layer 50 that is in contact with the carbon nanotubes 90 in the external skin layer 55.

14. The mechanical device 5 of Claim 10, wherein the carbon nanotubes 90 occupy about 1% to about 40% of the volume associated with the external skin layer 55.

15. The mechanical device 5 of Claim 14, wherein the carbon nanotubes 90 are oriented in the external skin layer 55 such that the external skin layer 55 exhibits a predetermined amount of enhancement in at least one mechanical property selected from the group consisting of Young's modulus, hardness, scratch resistance, and polymer creep.

16. The mechanical device 5 of Claim 10, wherein the outer surface 75 of the external skin layer 55 further comprises a superhydrophobic powder 100.

17. The mechanical device 5 of Claim 10, wherein the polymer composite 85 of the external skin layer 55 comprises one composition selected from the group consisting of polyimides, fluoropolymers, polyamides, polyesters, silicones, polyurethanes, epoxies, and polyacrylates.

18. A method 199 of making an external covering 20 for use with a mechanical device 5 that provides the external surface of the device 5 with skin-like qualities, the method characterized by the steps of:

providing a mold 200 having a cavity with a predetermined shape and at least one surface having a pattern selected as one from the group of a nano-funnel array, micro-funnel array, or combination thereof;

inserting a film 210 comprised of a polymer composite 85 with carbon nanotubes 90 embedded therein that has a first side and a second side into the cavity of the mold; the embedded carbon nanotubes providing the film with enhanced thermal conductivity; the first side of the film being in contact with the patterned surface of the mold's cavity;

applying 220 one selected from the group of heat, vacuum, pressure, or a combination thereof to the cavity or the film to form the film into the predetermined shape and to induce the formation of superhydrophobic cone-shaped projections on the first side of the film; the cone-shaped projections providing the first side of the film with superhydrophobicity;

cooling and removing 230 the shaped film from the mold; and

performing one step selected from the group consisting of adhering 240 the second side of the shaped film to a pre-shaped internal bulk layer to form the external covering and back-molding 330 the internal back layer to be in contact with the second side of the film.

19. The method 199 of Claim 18, further comprising the step of applying 215 a superhydrophobic powder 100 to the first side of the film prior to the film being inserted into the mold.

20. The method 199 of Claim 18, further comprising the step of annealing 205 the carbon nanotubes 90 prior to the nanotubes being embedded into the polymer composite 86 of the film.

21. The method 199 of Claim 18, further comprising the step 440 of opening a gap in the mold and injecting an in-mold coating into the gap to coat the first side of the film.

22. A method of making a prosthetic device 5 having an external surface providing skin-like qualities, the method characterized by the steps of:

forming an external covering 199 according to Claim 18, the external covering 20 having an internal bulk layer 50 and an external skin layer 55 with carbon nanotubes 90 embedded and aligned therein to provide enhanced thermal conductivity and multiple cone-shaped projections 80 located on at least one surface to provide superhydrophobicity; and

fastening 250 the internal bulk layer 50 of the external covering 20 to an internal endoskeleton 25.

23. The method of Claim 22, further comprising the step of applying 215 a superhydrophobic powder 100 to the external skin layer 55.

24. The method of Claim 22, further comprising the step of annealing 205 the carbon nanotubes 90 prior to the nanotubes 80 being embedded into the external skin layer 55.

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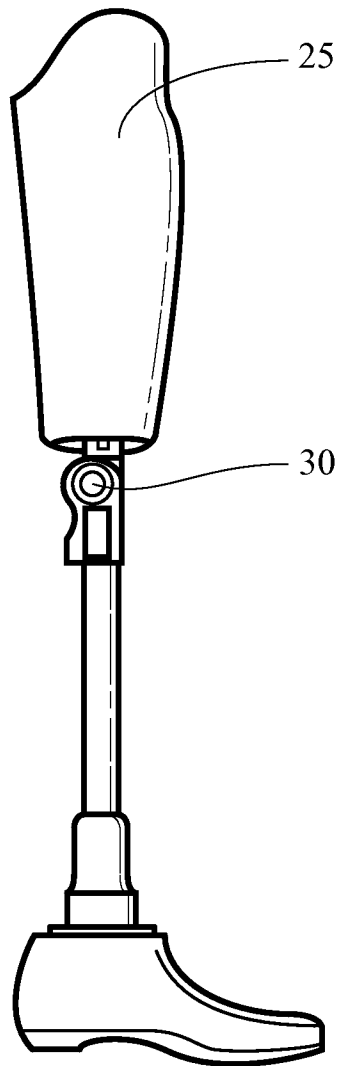


Fig. 1A

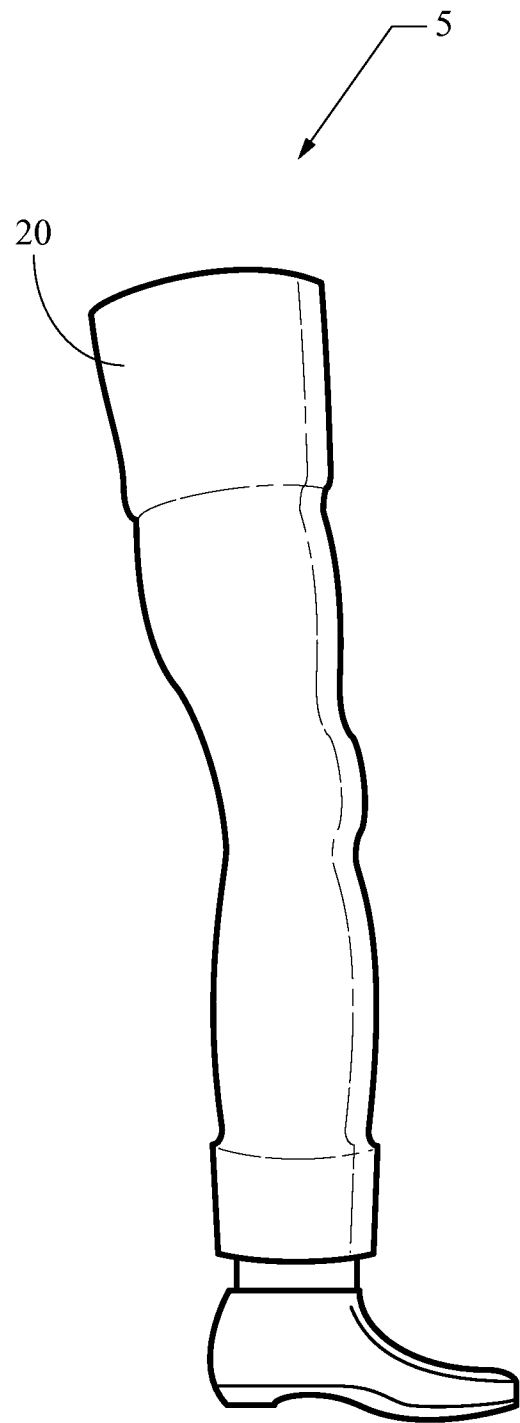


Fig. 1B

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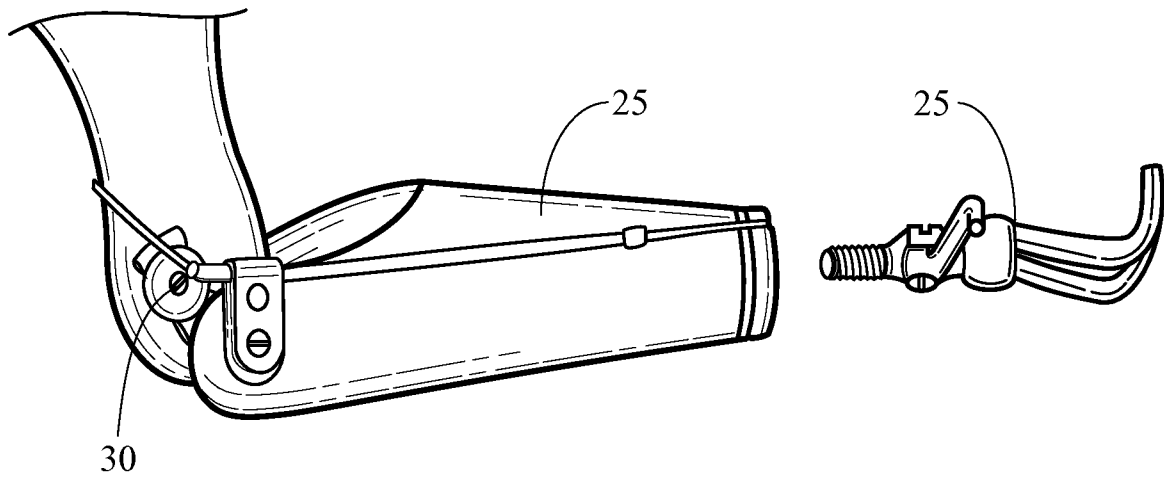


Fig. 2A

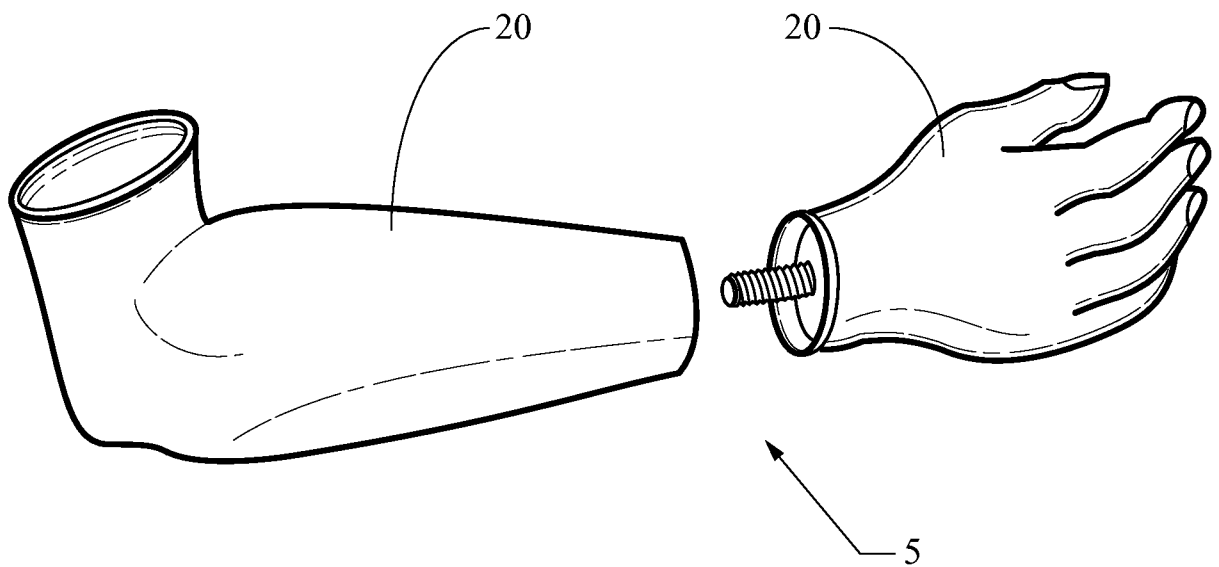


Fig. 2B

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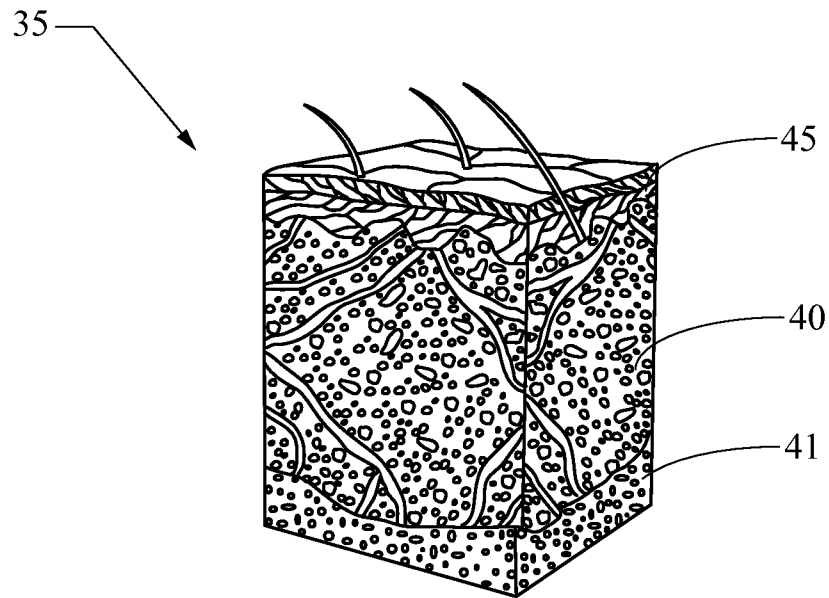


Fig. 3A  
(Prior Art)

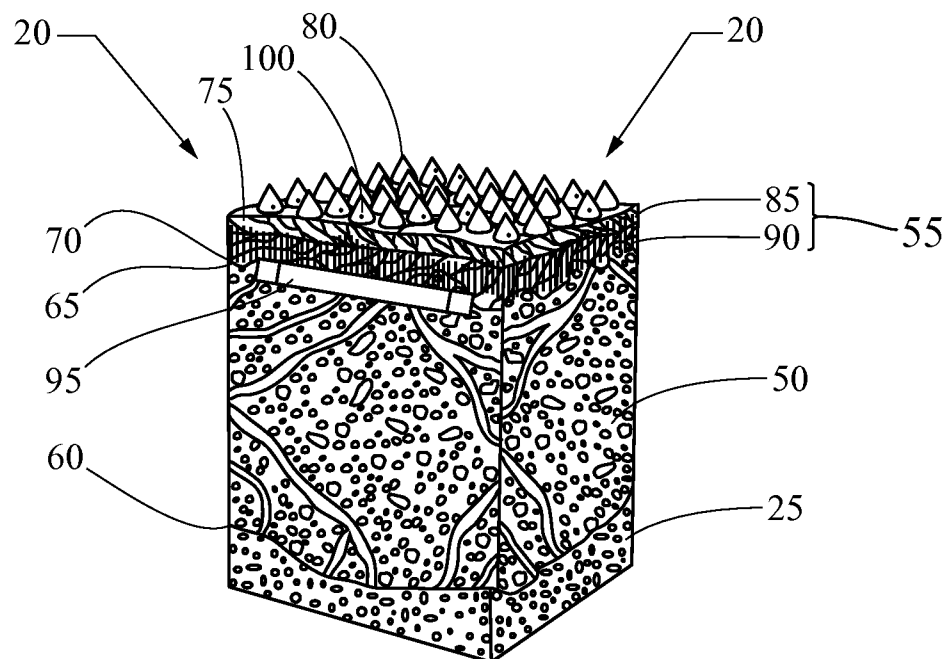


Fig. 3B

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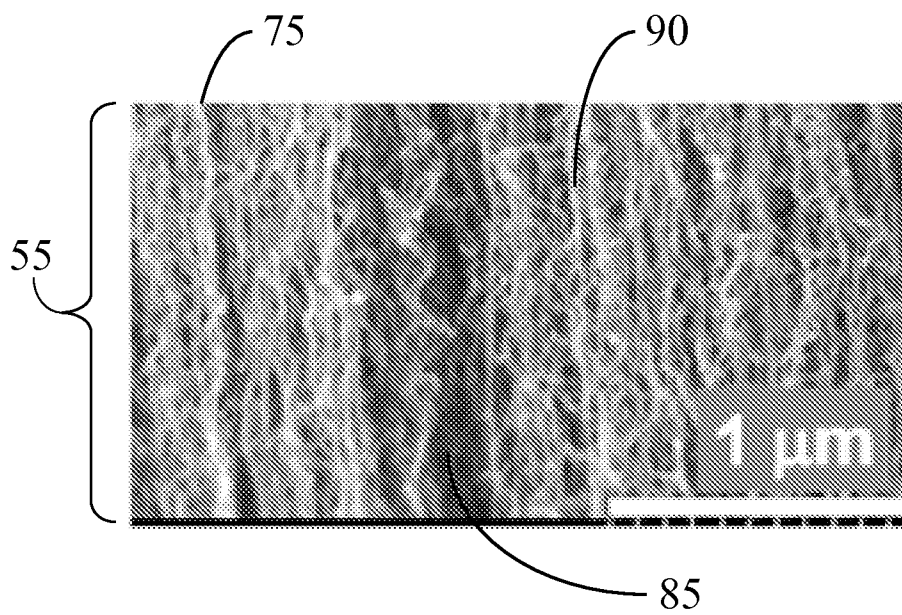


Fig. 4A

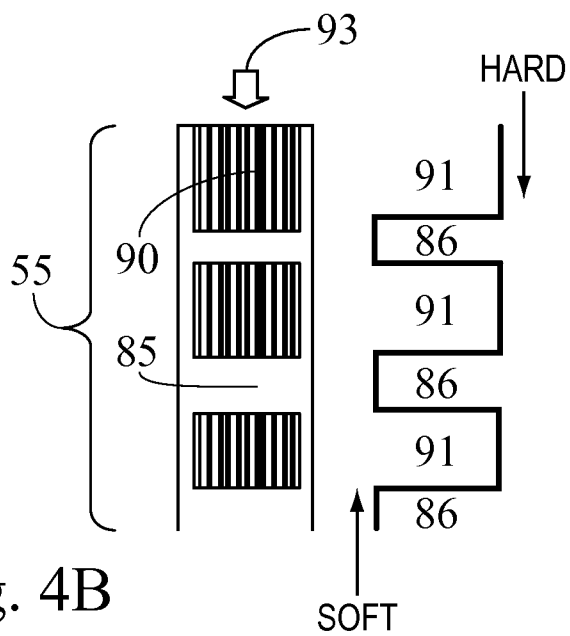


Fig. 4B

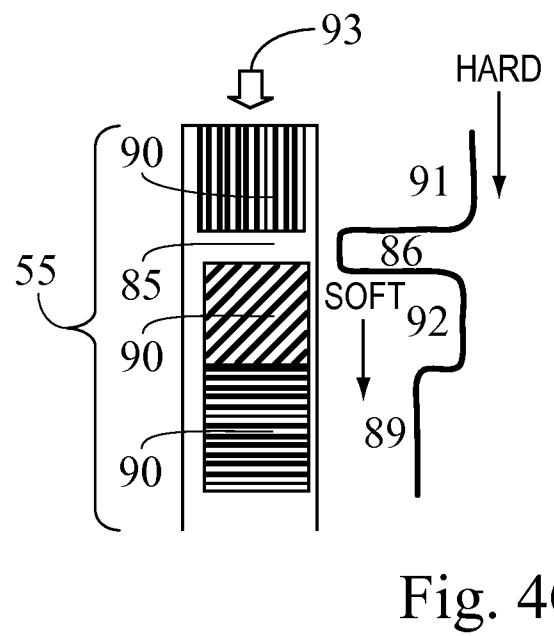


Fig. 4C

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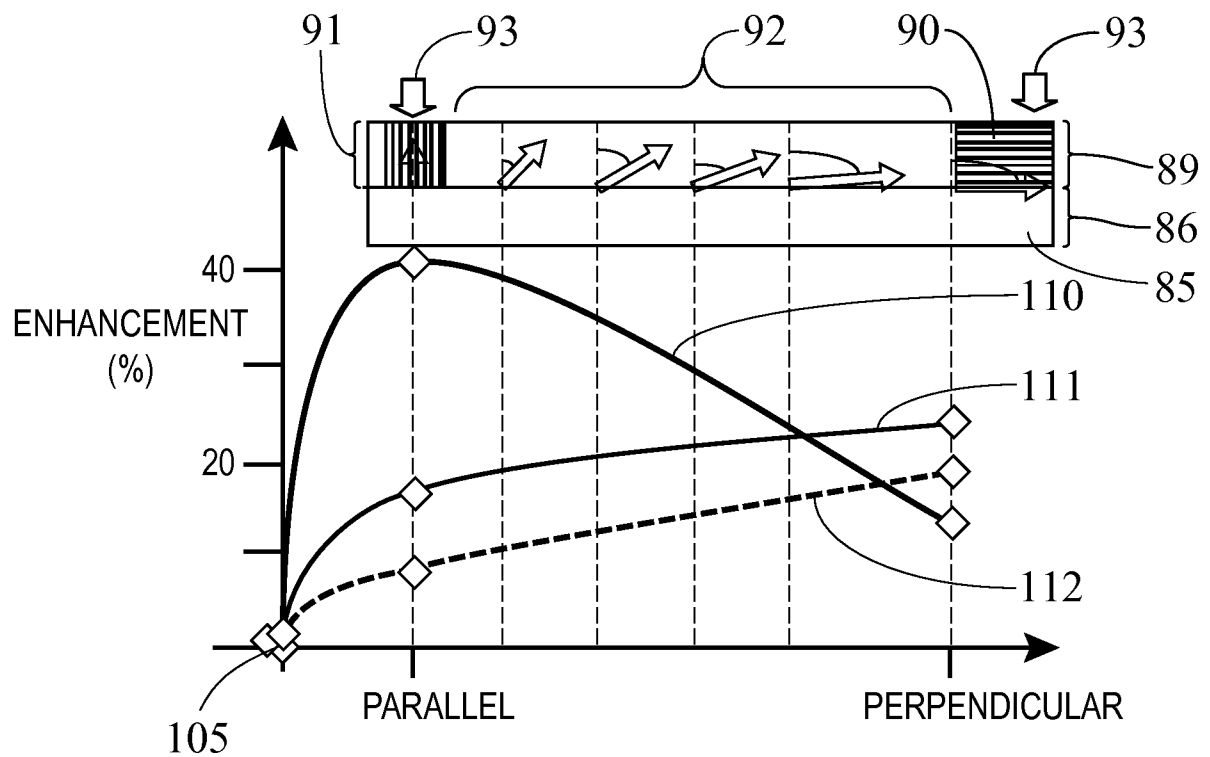


Fig. 5A

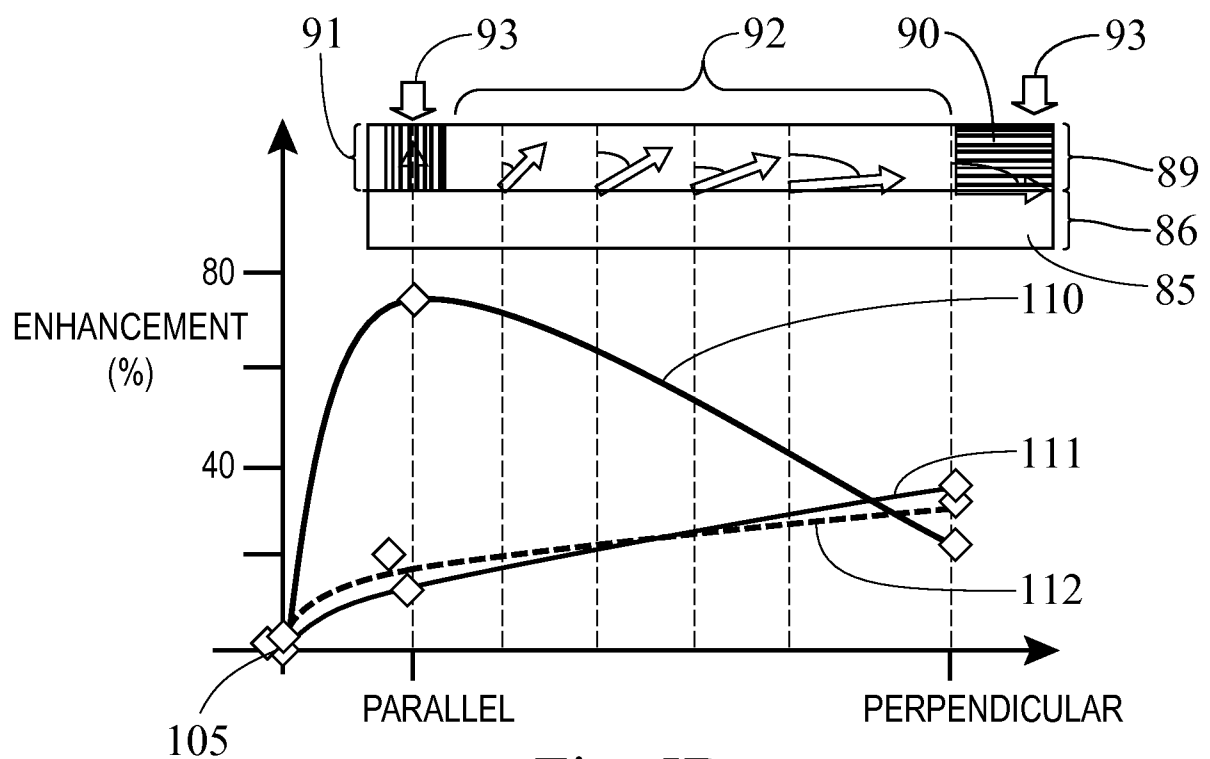


Fig. 5B

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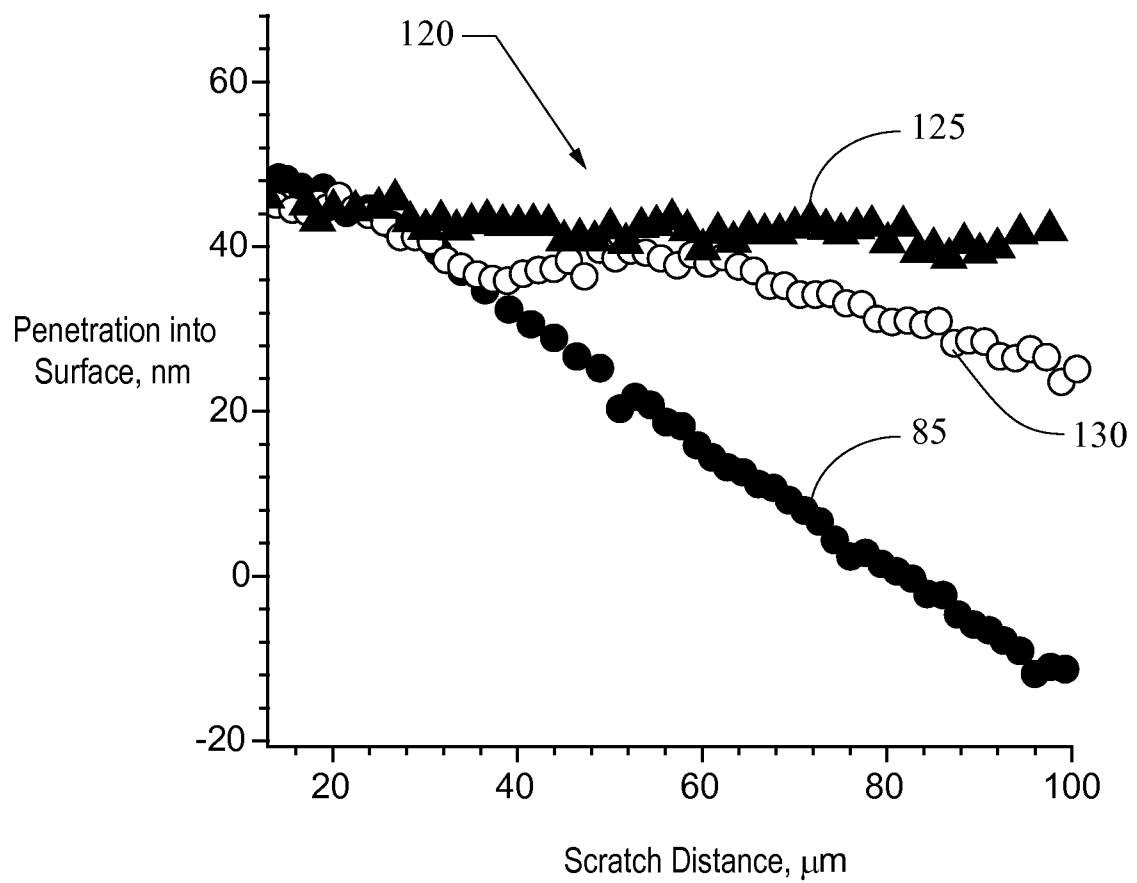


Fig. 5C

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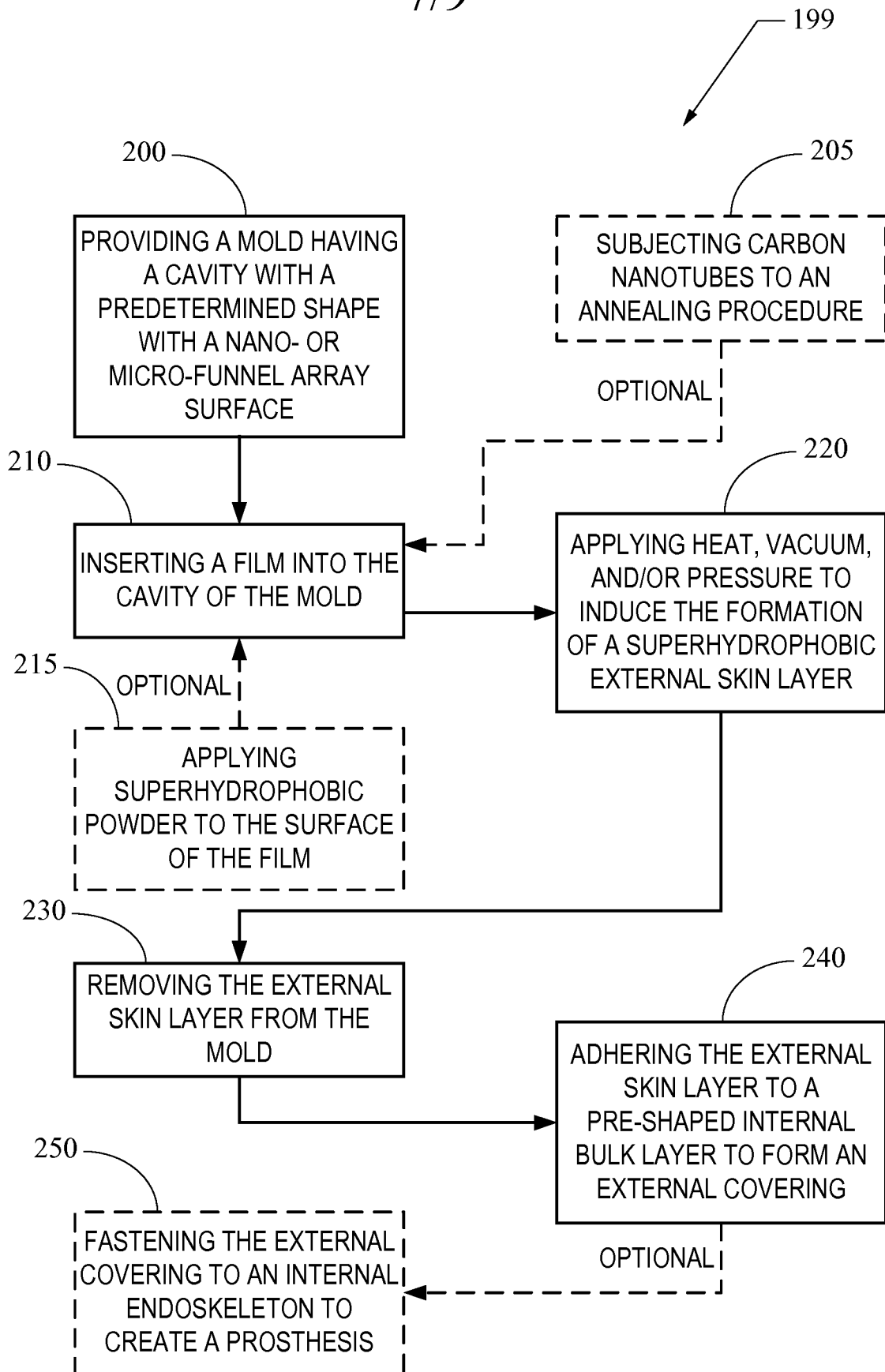


Fig. 6A

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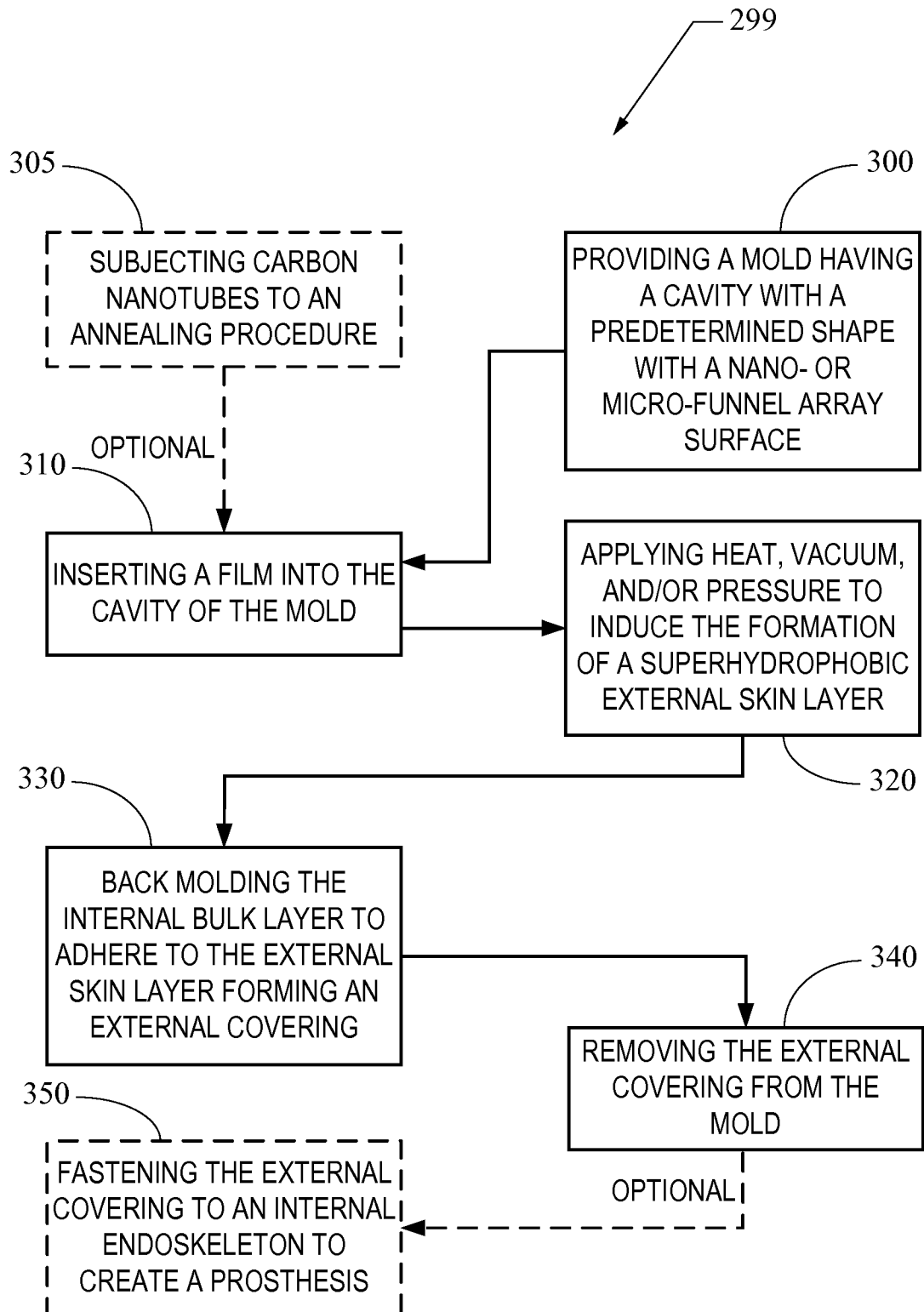


Fig. 6B

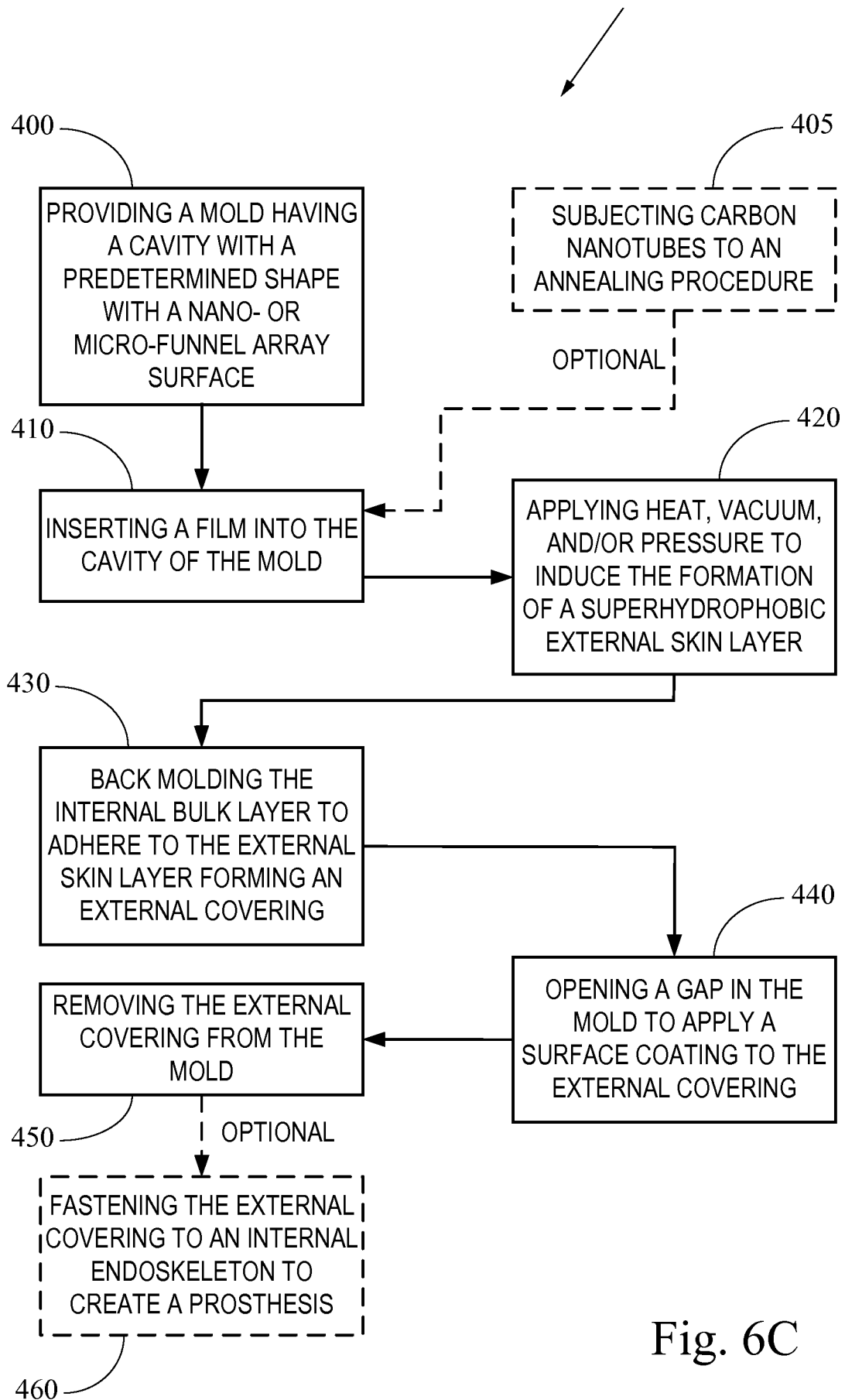


Fig. 6C

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2010/040511

## A. CLASSIFICATION OF SUBJECT MATTER

INV. A61F2/50 A61F2/76 A61F2/78  
ADD. A61F2/58

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)

A61F

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 practical, 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. |
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| Y         | <p>"FILMSkin Will Let People With Prosthetics Feel Heat, Cold And Touch"<br/>Science 2.0</p> <p>10 October 2007 (2007-10-10), XP002601898<br/>Retrieved from the Internet:<br/>URL: <a href="http://www.science20.com/news_account/filmskin_will_let_people_with_prosthetic_feel_heat_cold_and_touch">http://www.science20.com/news_account/filmskin_will_let_people_with_prosthetic_feel_heat_cold_and_touch</a><br/>[retrieved on 2010-09-22]<br/>the whole document</p> <p style="text-align: center;">-----<br/>-/--</p> | 1-24                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

24 September 2010

Date of mailing of the international search report

11/10/2010

Name and mailing address of the ISA/

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Authorized officer

Dennler, Samuel

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/040511

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                   | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | <p>"Artificial skin senses hot and cold"<br/>ABS Science</p> <p>10 March 2008 (2008-03-10), XP002601899<br/>Retrieved from the Internet:<br/>URL: <a href="http://www.abc.net.au/science/articles/2008/03/10/2185000.htm">http://www.abc.net.au/science/articles/2008/03/10/2185000.htm</a><br/>[retrieved on 2010-09-22]<br/>the whole document</p> | 1-24                  |
| Y         | <p>WO 03/013827 A1 (CREAVIS TECH &amp; INNOVATION<br/>GMBH [DE]; OLES MARKUS [DE]; SCHLEICH<br/>BERNHA) 20 February 2003 (2003-02-20)<br/>* abstract; figures 1-3<br/>page 4, lines 9-15<br/>page 5, line 18 - page 9, line 3</p>                                                                                                                    | 1-24                  |
| Y         | <p>US 2006/279191 A1 (GEOHEGAN DAVID B [US]<br/>ET AL) 14 December 2006 (2006-12-14)<br/>paragraph [0067]; figure 1</p>                                                                                                                                                                                                                              | 20,24                 |
| A         | <p>US 2009/018670 A1 (PUCHHAMMER GREGOR [AT])<br/>15 January 2009 (2009-01-15)<br/>paragraphs [0014], [0021] - [0026];<br/>figure 3</p>                                                                                                                                                                                                              | 1-24                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/040511

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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