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(54) **LOW FRICTION COATINGS FOR USE IN DENTAL AND MEDICAL DEVICES**

ÜBERZÜGE MIT GERINGER REIBUNG IN DENTAL- UND MEDIZINPRODUKTEN

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(56) References cited:

WO-A1-97/44278	**GB-A- 2 360 790**
JP-A- 1 083 252	**US-A1- 2003 144 155**
US-A1- 2004 109 823	**US-A1- 2004 173 378**
US-A1- 2004 173 378	**US-B1- 6 299 438**
US-B1- 6 299 438	

- **GAN ET AL: "Wear and Friction of Ni-P Electroless Composite Coating Including Inorganic Fullerene-WS2 Nanoparticles", ADVANCED ENGINEERING MATERIALS, vol. 4, no. 9, 27 September 2002 (2002-09-27), pages 686-690, XP055044505, ISSN: 1438-1656**
- **KATZ A ET AL: "Self-lubricating coatings containing fullerene-like WS2 nanoparticles for orthodontic wires and other possible medical applications", TRIBOLOGY LETTERS, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 21, no. 2, 1 March 2006 (2006-03-01), pages 135-139, XP019409599, ISSN: 1573-2711, DOI: 10.1007/S11249-006-9029-4**
- **TENNE R: "Inorganic nanotubes and fullerene-like structures", NATURE NANOTECHNOLOGY, NATURE PUBLISHING GROUP, LONDON, GB, vol. 1, 1 January 2006 (2006-01-01), pages 103-111, XP002463441,**

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Description

FIELD OF THE INVENTION

[0001] This invention relates to biocompatible dental and medical articles, such as orthodontic archwires, brackets, catheters, implants and needles, having a friction-reducing coating.

LIST OF REFERENCES

[0002] The following references are considered to be pertinent for the purpose of understanding the background of the present invention:

Chen et al, Adv. Eng. Mat. 4(9):686-690 (2002);
L. Rapoport et al, Wear 255:785-793 (2003);
Redlich et al., Am. J. Orthod. Dentofacial Orthop. 124, 69-73 (2003);
Tenne R. et al, Nature 360: 444-445 (1992);
U.S. Patent No. 5,288,230;
U.S. Patent No. 5,454,716;
U.S. Patent No. 5,958,358; and
U.S. Patent No. 6,299,438.

[0003] U.S. Patent Application 2003/0144155 A1 () Article in Advanced Ingineering Material 2002 "Wear and Friction of Ni-P Electroless Composite Coating Including Inorganic Fullerene-WS2Nanoparticles" (XP055044505.

BACKGROUND OF THE INVENTION

[0004] Many articles are currently produced bearing a low-friction coating, among them articles used in medicine and dentistry e.g. in orthodontics. Orthodontics is a dental specialty, which aims to bring about changes in the location of abnormally positioned teeth. This is achieved by application of continuous mechanical load (orthodontic force) on the tooth, which affects the periodontal ligament (PDL) and the alveolar bone surrounding the tooth. The applied force brings about remodeling of the PDL and the bone, which enables the transposition of the tooth. The orthodontic treatment has become very common in recent decades and also adults have begun seeking this treatment for esthetic and functional reasons.

[0005] The most common orthodontic technique consists of a rigid wire (also termed "*archwire*"), which is inserted into slots incorporated within special attachments (orthodontic brackets) being bonded on the teeth, as illustrated in **Fig. 1.** The basic principle of orthodontic appliances in the archwire technique is to apply mechanical forces on teeth so that movement will occur in every desirable spatial direction. The forces are applied during the various stages of treatment by a variety of appliances, which include several kinds of archwire, ligatures, brackets and bands.

[0006] Friction among appliances used for orthodontic correction of teeth is recognized by clinicians as a hindrance to tooth movement. Friction reduces the effective force, which is applied to the tooth from the wire. In the case of sliding mechanics, excessive friction, brought about by the angle between the wire and the slot of the bracket, slows tooth movement down substantially or even halts it. A frictional type force that resists the movement of the tooth and accompanies the sliding of a tooth along an archwire is referred to as resistance to sliding (RS).

[0007] There are a number of factors that may influence the RS directly and indirectly:

1. The archwire: size, shape, material and surface.
2. The bracket: material, size and shape of the slot and its edges, surface of slot and the angle formed between the wire and the slot.
3. Ligation of the wire in the slot: elastic module, metal wire ligature and self-ligating brackets.
4. Intraoral factors: saliva, plaque and corrosion.
5. Other factors: distance between teeth and direction of the applied force.

[0008] Over the years attempts have been made by researchers and manufacturers to reduce the friction. The problem was approached from different aspects:

1. Reduction of the size of the wire compared to the slot or the use of round wires, reduced friction to some extent but resulted in wire distortion that impaired the control of the direction of tooth movement.
2. Use of different metals (archwire or bracket) trying to reduce the coefficient of friction. The use of nickel-titanium

wire has a major advantage in arch alignment due to its shape memory quality but the friction on these wires is higher compared to stainless steel (SS) wires.

3. The method of ligating the wire to the slot can reduce friction. This was shown to be true with the self-ligating brackets at a 0° angle, but higher friction was recorded once the wire contacted the slot walls.

[0009] Coating thin films of various materials onto archwires has been previously suggested as another way to reduce friction and to improve their aesthetic appearance. U.S. Patent No. 5,288,230 describes applying a coating of diamond-like carbon (DLC) onto archwires to serve as a barrier to diffusion of nickel and chromium from the wire and also provide a hard, friction-reducing surface. U.S. Patent No. 5,454,716 describes a coating of a plastic-ceramic composite, which is aesthetically pleasing, but is susceptible to localized abrasion over time. Another method is described in U.S. Patent No. 6,299,438 and comprises applying a friction-reducing coating containing iridium or platinum to a metal and/or ceramic dental article which is first coated with an adhesion metal layer.

[0010] Another friction problem commonly encountered in dentistry is related to screw-type dental implants, between the implant and the bone walls into which the implant is inserted. Screw-type dental implants are made in two general types. The first type is a self-tapping implant that can be threaded into a pre-drilled bore in a jawbone without pre-tapping the bore. The second type is a non-self-tapping implant that requires pre-tapping of the bore. In either type, the implant has a generally cylindrical main body which bears one or more external screw threads on its outer surface. These external thread(s) engage corresponding internal thread(s) cut into the wall of the bore to provide initial stabilization of the implant in the bore.

[0011] The friction encountered by dental implants is proportional to the penetration depth of the implant into the bone, the diameter of the bore, and the hardness of the bone at the site of the bore. The torque that must be applied to insert the implant into the bore is proportional to the friction. High torque puts strains on the implant, on the tools used to place the implant in the bore, and on the bone. Furthermore, in cases where high torque is required to insert the implant, there is a greater risk of damage to the implant, the tools, and the bone. Consequently, there is a continuing need to design a screw-type dental implant which minimizes the torque needed to install it into living jawbone.

SUMMARY OF THE INVENTION

[0012] It would be clinically advantageous to reduce friction forces during orthodontic or other medical treatment. In orthodontics, unimpeded tooth movement may reduce the time needed for treatment, thereby reducing the risks of adverse effects of wearing orthodontic article on the teeth and surrounding tissues. Also in medicine, coating tissue penetrating devices with low friction coating may reduce tissue damage adjacent to these medical devices during the insertion procedure into tissues.

[0013] The present invention provides an article as disclosed in claims 1-14, being coated at least partially by inorganic fullerene-like (*IF*) nanoparticles or a composite containing such nanoparticles.

[0014] The present invention further provides methods, as disclosed in claims 15-20, for coating said article with inorganic fullerene-like (IF) nanoparticles or a composite containing such nanoparticles.

[0015] The present invention thus provides an elongated article at least part of it being coated by inorganic fullerene-like (*IF*) nanoparticles or composite containing *IF* nanoparticles. The inorganic fullerene-like (*IF*) particles are self-lubricating and thus reduce friction between the article and adjacent object, surface or tissue, as compared to uncoated article.

[0016] The article of the present invention is preferably made of metal, plastic, rubber or glass. More preferably, the article is made of metal.

[0017] An "*elongated article*" within the context of the present invention is an article extending preliminarily along one axis (i.e. length) while having smaller dimensions along the other perpendicular two axes (i.e. thickness and cross-section). In a preferred embodiment of the invention the elongated article has a cross-section in the range of about a centimeter or less, preferably of about several millimeters or less. Nevertheless, elongated articles with cross-sections larger than about a centimeter are also within the scope of the invention, as long as they are used in medicine or dentistry. Non limiting examples of elongated articles are needles, catheters and archwires.

[0018] In a preferred embodiment of the invention, the coated article is used in dentistry e.g. in orthodontic appliances or dental implants. For orthodontic uses the article is either circular or rectangular in cross-section and has the form of a wire or elongated hollow tube. In these uses at least part of the article of the invention is coated by friction reducing film comprising inorganic fullerene-like (*IF*) nanoparticles or composite containing *IF* nanoparticles.

[0019] The term "*wire*" as used herein includes, for example, an archwire used in orthodontic.

[0020] The term "*inorganic fullerene-like (IF) particles*" or "*inorganic fullerene-like (IF) nanoparticles*" within the context of the present invention covers hollow and non-hollow nanoparticles of transition metal chalcogenides and dichalcogenides, made up of single or multi-layers and having structures such as spheres, tubes, nested polyhedra, onion-like and the like.

[0021] A "*transition metal*" inlcudes all the metals in the periodic table from titanium to copper, from zirconium to silver and from hafnium to gold. Preferably, the transition metals are selected from Mo, W, V, Zr, Hf, Pt, Pd, Re, Nb, Ta, Ti, Cr and Ru.

[0022] A "*chalcogen*" as used herein refers to S, Se or Te.

[0023] The metal chalcogenides and dichalcogenides are preferably selected from TiS_2, $TiSe_2$, $TiTe_2$, WS_2, WSe_2, WTe_2, MoS_2, $MoSe_2$, $MoTe_2$, SnS_2, $SnSe_2$, $SnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, GaS, GaSe, GaTe, InS, InSe, HfS_2, ZrS_2, VS_2, ReS_2 and NbS_2. More preferably, the metal chalcogenides and dichalcogenides are selected from WS_2 and MoS_2.

[0024] Inorganic fullerene-like WS_2 (*IF*-WS_2) was first reported by Tenne and coworkers in 1992 [Tenne R. et al, Nature 360: 444-445 (1992) and U.S. Patent No. 5,958,358]. It was shown that under a certain reducing and sulfidizing atmosphere at elevated temperatures, tungsten oxide nanoparticles could fold and form nested WS_2 fullerene-like nanostructures with layers that resemble an onion. The size of these nanoparticles range from tens to several hundreds of nanometers, depending on the WO_3 precursor's size.

[0025] Surprisingly, the inventors have found that *IF* particles are biocompatible. Consequently, and in view of their superior tribological properties, as compared to same particles in platelet form [L. Rapoport et al, Wear 255:785-793 (2003)], these biocompatible *IF* particles may be used in biological systems in humans to alleviate friction problems. Consequently, the present invention provides a biocompatible article, preferably made of metal, at least part of it being coated by friction reducing film comprising inorganic fullerene-like (*IF*) particles or composite containing *IF* particles.

[0026] "*Biocompatible article*" is defined for purposes of this description as article that can be used in animals, particularly humans without a significant adverse biological (e.g., toxic, inflammatory, carcinogenic, or imnunogenic) host response (e.g., foreign body reaction, autoimmune disease, necrosis, apoptosis) whether delayed or immediate.

[0027] A preferred embodiment of the present invention also provides an improved screw-type dental implant that reduces the torque required to install the implant by reducing the friction between the implant and the sidewalls of the bore, at least a portion of the implant being coated by friction reducing film comprising inorganic fullerene-like (*IF*) particles or composite containing *IF* particles.

[0028] The term "*composite*" as used herein refers to solid material made from two or more components. One component is often fibers or particles, such as graphite fibers, BN-whiskers and *IF*-nanoparticles, that give the material its tensile strength, while another component (called a matrix), such as Ni-P, polyurethane and epoxy, binds the fibers or particles together. Non-limiting examples of composite according to the present invention are Ni-P-*IF*-nanoparticles any metal film, like Pt containing *IF*-nanoparticles, polymer (e.g. polyurethane or polypropylene) or epoxy containing *IF*-nanoparticles. or a sol-gel glass containing *IF*-nanoparticles.

[0029] The term "*friction-reducing film*" refers to a film or layer of an article capable to reduce the surface friction coefficient of that article, as measured with a ball-on-flat device by at least 20% when compared to the friction coefficient of the uncoated article.

[0030] The article of the invention being coated at least partially with a friction reducing film is used in dentistry and medicine and is selected from all types and sizes of orthodontic archwires, all types of orthodontic brackets, dental implants, bands, all types of bonded or banded orthodontic attachments and, palatal expanders used to orthodontically expand lower and upper dental dentitions. The friction reducing film can be also used to reduce friction in mobile functioning native or artificial human joints including temporo-mandibular joint, knee, ankle, elbow etc and also in hip replacement. Coating needles or catheters, which penetrate human tissues, with the friction reducing film of the invention will signifcantly reduce tissue damage adjacent to these medical devices during the insertion procedure. Further uses of low friction medical instruments are feeding oral and nasal tubes as well as the various tubes used for laparoscopic surgeries. The articles may be made of any metals suitable for use in dental and medical devices, for example stainless steel, iridium, platinum, palladium, rhodium, rhenium, alumina, zirconia, nickel-titanium, gold, silver, titanium, titanium-molybdenum alloy (TMA), beta-titanium and blends or alloys of these.

[0031] The friction reducing film comprises biocompatible *IF* nanoparticles or composite containing such nanoparticles, capable of reducing the surface friction of the coated article (compared to the uncoated article) so that metal pieces e.g. pieces of the dental article which are connected together and cooperate with each other, e.g., archwires and brackets, can slide past each other more easily, thereby allowing for easier and more precise adjustment by the orthodontist or dentist. The coating preferably also has the properties of being resistant to mechanical wear and sufficiently inert to resist degradation in the environment of the mouth.

[0032] In order to utilize the properties of the *IF*-nanoparticles to reduce the friction in biological systems, the inventors developed a method for reducing friction between an article used in medicine or dentistry and adjacent surface, tissue or object, by coating at least part of the article's surface by inorganic fullerene-like (*IF*) nanoparticles or composite containing such nanoparticles.

[0033] One of the effect of the present invention is to reduce friction between a dental article and other articles or the tooth, said article being selected from dental implant, orthodontic wire, orthodontic bracket, band, bonded or banded orthodontic attachment, palatal expanders.

[0034] It should be noted that the present invention is preferably adapted for coating wires and similar tubular structures that are characterized by different morphologies in comparison to flat substrates.

[0035] The present invention provides also a coating method as disclosed in claim 15.

[0036] According to the invention, the method comprises prior to contacting the article with the plating solution exposing the article to a surface pre-treatment procedure. Preferably, the pre-treatment procedure is carried out with an etching acidic solution, for example HF etching solution.

[0037] According to another preferred embodiment of the invention, the method comprises one or more additional deposition steps prior to said contacting to form intermediate layers between the article and the outer, friction reducing film.

[0038] According to a preferred embodiment of the invention, the method further comprises annealing the coated article at high temperature.

[0039] Preferably, the article is a metallic wire. More preferably, the wire is a wire used in orthodontic appliances and is usually made of stainless steel, iridium, platinum, palladium, rhodium, rhenium, gold, silver and blends or alloys of these.

[0040] In a preferred embodiment of the invention, the article is also exposed to e-beam deposition of Ni-Cr and/or Ni before the deposition of the friction reducing film.

[0041] The friction reducing film may be applied by any technique which is useful for depositing metallic coatings onto metallic substrates, for example, electroless deposition and electrodeposition, sputtering, chemical vapor deposition, ion beam enhanced deposition, plasma-assisted vapor deposition, cathodic arc deposition, ion implantation and evaporation, most preferably being electroless deposition and electrodeposition.

[0042] In a preferred embodiment where electroless deposition is applied, the plating solution comprises Ni or Co, phosphate or borate salt, reducing agent e.g. citrate, and surfactant and the article obtained by the method of the invention is coated with a friction-reducing film comprising composite of Ni-P, Co-P, Ni-B or Co-B and *IF* nanoparticles.

[0043] In another embodiment of the invention the article is coated with a polymer (e.g. polyurethane or polypropylene) or epoxy coating.

[0044] In a further embodiment of the invention, a sol-gel glass coating is applied on the article.

[0045] According to one embodiment of the invention, the article is coated with *IF*-nanoparticles. For implementing this embodiment, nanoparticles powder, such as *IF*-WS_2 powder, may be burnished with cloth for 15 minutes and then the article may be also burnished with the cloth until a thin coating of the *IF*-WS_2 is applied on the article, which serves as a self-lubricating coating.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting examples only, with reference to the accompanying drawings, in which:

Fig. 1 is a photograph illustrating the orthodontic setup of a fixed orthodontic appliance.

Fig. 2 is a SEM magnification x 12000 of Ni-P coating on SS wire.

Figs. 3A and **3B** show TEM images of single *IF*-WS_2 nanoparticles. after ultrasonic dispersion within a Ni-P matrix after 2 minutes of sonification and one hour of plating activity, respectively. **Figs. 3C** and **3D** show an enlarged TEM image of the *IF* where the layers are observed with no apparent damage.

Fig. 4 is an optical micrograph of the surface of a Ni-P-*IF*-WS_2 film, after 100 cycles of dry friction.

Fig. 5 shows optical micrographs of the surface of Si_3N_4 ball after the friction with Ni-P-*IF* coating using Mouth Kote fluid (A) - Before cleaning, (B) - After cleaning.

Fig. 6 is a graph showing the friction coefficient of the orthodontic wire vs. number of cycles, compared to a wire coated with Ni-P-WS_2 composite.

Fig. **7A** is a graph of force (N) vs. displacement (mm) in non coated SS wire, taken at 0° angle of contact between the bracket and the wire; average force is 1.32N (STANDARD DEVIATION (SD)) =0.12).

Fig. 7B is a graph of force (N) vs. displacement (mm) in coated wire, taken at 0° angle of contact between the bracket and the wire, tested on the same bracket; average force is 1.10N (SD=0.06).

Fig. 8A is a graph of force (N) vs. displacement (mm) in non coated SS wire, taken at 5° angle of contact between the bracket and the wire; average force is 2.95N (SD=0.09).

Fig. **8B** is a graph of force (N) vs. displacement (mm) in coated wire, taken at 5° angle of contact between the bracket and the wire, tested on the same bracket; average force is 1.58N (SD=0.25).

Fig. 9A is a graph of force (N) vs. displacement (mm) in non coated SS wire, tested in dry mode at 10° angle of contact between the bracket and the wire; average force is 4N (SD=0.19).

Fig. 9B is a graph of force (N) vs. displacement (mm) in non coated SS wire, tested in wet mode at 10° angle of contact between the bracket and the wire; average force is 3.3SN (SD=0.21).

Fig. 9C is a graph of force (N) vs. displacement (mm) in coated wire, tested in wet mode at 10° angle of contact between the bracket and the wire, tested on the same wet bracket; average force is 1.57N (SD=0.23).

Fig. 10 is a photograph of the bracket-mounting apparatus.

Fig. 11 is a photograph of an angulation device with an aluminum plate screwed in the 10° angle slot.

Fig. 12 is a photograph showing an orthodontic wire inserted into the bracket slot and ligated by an elastic module. The wire is connected on the top to the load cell and on the bottom to the 150g weight.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0047] The present invention provides an article for use in medicine or dentistry, preferably made of metal, at least part of its surface being coated by friction reducing film comprising inorganic fullerene-like (*IF*) nanoparticles or composite containing such *IF* nanoparticles.

[0048] The article may be, for example, an elongated article such as a metallic wire e.g. orthodontic archwire or elongated medical article e.g. needle, catheter, etc.

[0049] The present invention further provides methods for coating the articles with a friction-reducing film which comprises *IF* nanoparticles. or composite containing such nanoparticles.

[0050] When the article is a dental article, it may comprise a metallic article which is placed temporarily or permanently in the mouth of an individual. Such articles include, for example, orthodontic appliances such as archwires or screw-type dental implants. The orthodontic wires or dental implants may be comprised of any metals suitable for use in dental devices, for example stainless steel, titanium, titanium-molybdenum alloy (TMA), beta-titanium, nitinol, alumina, zirconia, nickel-titanium, and alloys and blends of these materials. Beta-titanium, stainless steel and nickel-titanium alloys are currently preferred archwire materials.

[0051] Materials useful for the friction-reducing film include hard, relatively inert metals which do not tend to form oxides in the environment of the mouth, biocompatible *IF* nanoparticles. and composites with such nanoparticles. The coated wire of the invention also may include one or more additional intermediate layers between the wire and the outer, friction-reducing film. The intermediate layer(s) preferably comprise a metallic material selected from the group consisting of Ni and Ni-Cr.

[0052] One method of applying the friction reducing film is by incorporating the *IF* nanoparticles into a coating by composite electroless deposition. Electroless plating has gained popularity since the beginning of the last century when it was first introduced, due to the production of coatings with excellent corrosion, wear and abrasion resistance. Electroless plating is a chemical process of oxidation and reduction by which a metallic ion is reduced from an aqueous solution containing a reducing agent onto a surface having a catalytic site with no need to transfer a current. Of the variety of metal ions that are in use, nickel and cobalt have proven supremacy in corrosion and wear resistance when deposited as nickel phosphorus (Ni-P), cobalt phosphorus (Co-P), or mixtures of Co-P or Ni-P with other transition metals such as for example Co-Ni-P, Co-Rh-P, Co-W-P or Co-Fe-P. The incorporation of *IF*-WS_2 nanoparticles into Ni-P matrix was carried out by a method similar to that reported by Chen et al [Chen et al, Adv. Eng. Mat. 4(9):686-690 (2002)].

[0053] Another way of coating an article with a friction reducing film is by electrochemical deposition. In this way the article is first exposed to a surface pre-treatment procedure. In the next step, the article is immersed in a metal solution and a current is applied. A similar solution containing *IF* nanoparticles is then prepared by sonication and the article is immersed in this solution and a current is applied. Alternatively, the article is first immersed in a metal solution, such as Cr or Ti and then in the next step is immersed in another solution of Ni-P or Cr containing the *IF* nanoparticles.

[0054] The metal solution for the electrochemical deposition may be any metal solution. For example, the metal may be Ni, Pt, Co, Cr, Fe, or alloys thereof.

[0055] In a preferred embodiment of the invention the article is coated with a polymer (e.g. polyurethane or polypropylene) or epoxy coating. In this embodiment, the polymer is heated until a non-viscous polymer is obtained and then *IF*-nanoparticles are added. In the next step, the article is painted with the polymer or immersed in the polymeric solution. Then the polymer is treated by curing (radiation) or by cross-linking (e.g. with UV light).

[0056] In a further preferred embodiment, a sol-gel glass coating is applied on the article.

[0057] Another way of coating an article with a friction reducing film is implemented by burnishing nanoparticles. powder with cloth for a few minutes and then burnishing the article with the cloth until a coating of the nanoparticles is applied on the article, which serves as a self-lubricating coating.

Electroless Ni-P coatings on stainless steel (SS) orthodontic wires

[0058] **Fig. 2** shows a smooth, homogenous film of electroless Ni-P on a stainless steel wire. The scotch bond test caused peeling of the coating, as opposed to a same test carried on a stainless steel plate coated with similar Ni-P film by electroless deposition, indicating poor adhesion to the wire substrate. The SEM images of the two substrates showed different microscopic morphology in spite of having the same SS composition. This difference in the surface morphology is suggested to be the cause to the poor adhesion of Ni-P film exhibited by the wires as opposed to plates.

Electroless plating composite of Ni-P with *IF*-WS_2 particles

[0059] Preparation of electroless bath: enabling a mixture of *IF*-WS_2 particles (or other desired IF particles) into the electroless Ni plating solution required the nanoparticles dispersion within the electroless plating bath. This was achieved by agitating a dispersion of the WS_2 nanoparticles in the electroless bath (commercially available solution sold under the name Enplate Ni-425, Enthone Inc.) by ultrasonic stirrer and also by the use of suitable surfactants. Among the series of surfactants used, i.e. anionic (SDS-sodium dodecyl sulfate), cationic (CTAB-cetyl trimethyl ammonium bromide) and non-ionic (Triton-x), CTAB seemed to show the best results.

[0060] **Figs**. **3A** and **3B** show TEM images of single *IF*-WS_2 nanoparticles after ultrasonic dispersion within a Ni-P matrix after 2 minutes of sonification and one hour of plating activity, respectively. **Figs**. **3C** and **3D** show an enlarged TEM image of the *IF* where the layers are observed with no apparent damage.

[0061] The electroless reaction was carried out first by treating the wire with an HF solution, in order to cause pitting of the substrate and consequently mechanically enhance the adhesiveness of the coating to the wire substrate. In a second step the wire was subjected to electroless coating in a commercially available plating bath containing essentially *IF* particles, Ni and phosphate, to obtain a wire coated with composite Ni-P-*IF*-WS_2 film that had adequate adhesive strength to the wire surface (adequate adhesive strength as measured by the scotch-bond test). The thickness of the Ni-P-*IF*-particles film obtained by the method of the present invention is between about 0.3 microns to about 50 microns, more preferably between about 1 to about 10 microns.

Electroless plating composite of Co-P with *IF*-WS_2 particles

[0062] In a similar manner the inventors obtained a composite film of Co-P with *IF*-WS_2 particles, by electroless plating. The plating solution (pH 6.85) consisted of 0.3 M sodium citrate ($Na_3C_6H_5O_7$), 0.1M sodium hypophosphate and 0.1 M ammonium chloride (NH_4Cl). The concentration of cobalt (II) chloride ($CoCl_2$) was increased up to 0.1 M. The hydrazine (N_2H_4) concentration was increased up to 0.3 M. The pH was controlled by increasing the sodium hydroxide (NaOH) concentration up to 1.25 M.

[0063] *IF*-WS_2 particles were dispersed in the Co electroless bath by using an anionic surfactant, for example SDS (sodium dodecyl sulfate). A uniform film of Co-P or Co (depending on the existence or absence of sodium hypophosphate in the plating solution) with the *IF* particles was obtained.

Electrochemical plating film of Co with *IF*-WS_2 particles

[0064] A film of Co with *IF*-WS_2 particles was obtained by electrochemical plating. A stainless-steel plate (5x5 mm^2) was cleaned first by immersion in HF (20%) solution for 2 min. The plate was subsequently rinsed carefully in water and dried under N_2 gas stream. In the next step, the plate was immersed in a solution containing 40 ml $CoCl_2$ 1M (and optionally 40 ml $NiCl_2$ 1M) and 0.2 ml acetic acid was added to the solution to bring the pH to 3.5. A current of 1 mA was applied on the plate which served as cathode with Pt gauge as an anode. The stainless steel plate was rinsed and immersed in a similar solution but now containing 3 wt% of *IF*-WS_2, which was prepared by sonication. A current of 1mA was applied for 20 second. A black film was obtained. The overall thickness of the film was about 6 micron.

Sol gel glass coating with *IF*-WS_2 particles

[0065] A mother solution of Zirconia is prepared. Glacial acetic acid (3ml) is slowly added to 10 ml of zirconia tetrapropoxide ($Zr(OC_3H_7)_4$, TPOZ) and stirred for 30 minutes. Then 20 ml of *n*-propanol (C_3H_7OH) is added to the solution, which is further stirred for 15 minutes at room temperature. The solution is hydrolyzed with 4 ml of 50% diluted solution of acetic acid in deionized (DI) water. Following this step, the solution is stirred for another 30 minutes at room temperature, filtered, and stored in a refrigerator for up to 4 days. The solution is transparent and its color pale yellow.

[0066] In the next step, alcoholic suspension of the *IF*-WS_2 nanoparticles is prepared by sonication of 10 mg of the nanoparticles and is added dropwise to the stirred mother solution. After that the articles are immersed in the suspension and after withdrawing (dip coating) and drying are annealed in 40 °C for an hour. The final step is annealing of the articles at 300 °C in inert gas atmosphere.

Friction and wear testing

[0067] The tests were performed using a ball-on-flat device with a sliding velocity of 0.2 mm/s and a load of 50 gr. A bearing ball with a diameter of 2 mm was used as a counter body. Dry and wet friction with paraffin oil lubricant were carried out during 50-200 cycles. Optical magnification of micrographs is x240.

[0068] The surface of Ni-P-*IF*-WS_2 coating with a wear track after 100 cycles of dry friction is shown in **Fig. 4.**

[0069] In order to simulate the friction behavior of the coatings in the mouth at definite fluid medium, some drops of Mouth Kote (oral moisturizer) have been fed into the interface between the steel ball and the coating. In this experiment the ball used was made of silicone nitride. Corrosion tracks on the surface of the ball were not observed, as can be seen in **Fig**. **5A**. The *IF* particles are observed on the surface of the silicon nitride ball before cleaning with hexane. No wear track and particles on the surface of the ball were observed after the cleaning, as can be seen in the photograph in **Fig**. **5B**. In another test the inventors compared the friction coefficient of an uncoated orthodontic wire substrate to that of a wire coated with a composite of Ni-P-WS_2. The graph in **Fig. 6** shows the results of 30 cycles of this test, from which it is evident that after the first cycle the friction coefficient of the uncoated wire was 0.1 and that of the coated wire was 0.08, while after 30 cycles the uncoated-wire friction coefficient was 0.25 and that of the coated wire was 0.05.

Instron testing

[0070] The coated wires were compared to uncoated wires at conditions simulating the movement of the tooth and bracket on the wire in the mouth, by using the Instron assembly. The tests were set at 3 different angles of contact between the bracket and the wire. From the results presented in Fig. 6 it was obvious that a run-in period was needed before testing the wires on the Instron. The run-in period of the wire was done by repeated back and forth movements of the wire in a bracket slot before comnecting the wire to the Instron. A different bracket was used for the Instron testing. Data is presented in Table I below and comparative graphs in **Figs. 7-9** showing the relation between force and displacement of brackets where the peak indicates the maximum force needed to begin movement of the bracket on the wire (static friction).

Table I: Summary of Instron testing. Results or Force are in N ± SD.

ANGLE **COATING**	**0°**	**5°** Uncoated wire tested first	**5°** Coated wire tested first	**10°** Uncoated wire tested first	**10°** Coated wire tested first
Non coated wire	1.32±0.12	2.95±0.09	2.64±0.16	4.00±0.1 9 Dry 3.35±0.2 1 wet	2.76±0.26 wet
Ni-P + *IF* coated wire	1.10±0.06	1.58±0.25	1.61±0.18	1.57±0.23 wet	1.85±0.21 dry 1.85±0.31 wet

[0071] The highest angle of 10° was tested in the dry and wet mode. DI water was used instead of the Mouth Kote lubrication fluid due to the possible damage to the Instron equipment. Angles 5° and 10° were repeated in a reverse order for the purpose of investigating the effect of residual nanoparticles remaining in the bracket slot.

[0072] The Instron results show a substantial reduction in the friction resistance to sliding at the different angles that were tested. At an angle of 0° the reduction of friction was 17%. As the angle grew to 5°, the reduction rate grew to 46% and the 10° angle showed a 54% reduction of friction compared to the uncoated wire. Without being bound to theory, the mechanism by which this reduction is achieved may be explained by the theories suggested by Rapoport et al [Rapoport et al., Wear 255, 785-793 (2003)]. At the first stage when there is no angle between the slot and wire, the *IF* nanoparticles act as spacers and reduce the number of asperities that come in contact resulting in a lower coefficient of friction. As the angle grows the load at the edges of the slot increases causing the higher friction levels on the uncoated wire. It is probably at this point on the coated wire that the exfoliation of the nanoparticles occurs, resulting in the dry lubrication of the sliding. The higher load at this point brings the asperities in close contact causing the saliva to be squeezed out of the gap between the wire and slot, relying on the dry lubrication properties of the materials in contact to allow the sliding. When the two materials are stainless steel, as is with the uncoated wire, the friction coefficient is higher. When *IF* particles are in the interface under high loads, the sliding occurs within these sheets reducing the coefficient of friction.

Conclusions

[0073] The tests, carried out on SS plates, resulted in a composite coating of an electroless Ni-P matrix and *IF*-WS_2 nanoparticles dispersed within this matrix. The dynamic coefficient of friction was reduced from 0.6 on the stainless-steel substrate to 0.06 on the coated substrate. Comparing the tribological testing results of the plate substrate to the orthodontic wire shows that the orthodontic wire has an initial low dynamic coefficient of friction (0.1) even though they are composed of the same stainless steel substrate. This perhaps is attributed to the finishing process done by the manufacturer and is evident by the different surface morphologies seen in the SEM images. In spite of the low coefficient of friction, the orthodontic force that is needed in order to move a tooth along an archwire is still much higher than the biological requirement due to the friction force that develops during this movement. The friction coefficient of the wire increases dramatically when the load increases, which was indeed the case when the orthodontic wires were used in realistic conditions (by tilting the bracket). For this reason it is desirable to achieve a reduction in the friction coefficient of the wire. The coating of the wire with the composite Ni-P-*IF*-WS_2 reduced the friction coefficient to 0.05 after a run-in period. When the uncoated wire was tested in cycles, the friction coefficient was elevated to 0.25. This could mean that the force needed for orthodontic movement grows with time on the uncoated wire and is reduced with time on the coated one.

[0074] Instron tests were carried out in order to simulate the actual type of forces that develop during the orthodontic tooth movement. The Instron simulates the tilt in the wire with respect to the bracket and consequently the entire load is exerted on a small area of the bracket (on the corners), resulting in much higher friction. These tests resulted in the reduction of friction on the coated wire, a reduction that is pronounced with the elevation of the angle between the wire and the slot. At an angle of 10°, the force needed to move the bracket along the archwire was 54% lower on the coated wire. Due to the tipping and uprighting type of movement that is encountered during orthodontic treatment, this type of lubrication is most desirable because the main problem of resistance to sliding is found at the angels higher than the critical contact angle.

[0075] Tribological tests in the wet mode using a saliva substitute resulted in increased friction coefficients for both coated and uncoated SS plates tested with a tempered steel ball. When the wires were tested on the Instron in the wet mode, using DI water and SS brackets, a reduction in the force (friction) was recorded. This difference is attributed to the corrosion that developed on the tempered steel ball tester and to the fact that a different type of fluid was in use. The reduction observed with the wire and bracket in the Instron was attributed to the lubrication potential of the DI water and the short duration of the test.

[0076] The method developed here for coating the orthodontic archwire substrate was aimed at overcoming the poor adhesive strength of the coating to the wire, compared to the SS plates. Use of Ni or Ni-Cr + Ni by e-beam evaporation as an initiator of the electroless process was not sufficient. A conditioning step of etching the substrate by HF was needed for increasing the retention of the coating to the wire. The reason for the difference between the SS plate and the orthodontic wire is probably due to the finishing process and the flexibility of the wire, which can affect the bonding force between the coating and the wire.

[0077] The coatings of the invention may be applied to other orthodontic materials as well. A self-ligating bracket, for example, should show even lower friction levels when the coating is in use. Moreover, this coating may be utilized in other biological systems where friction is a problem as in temporomandibular disorders or in hip replacements.

EXPERIMENTAL WORK

[0078] Experiments were carried out on orthodontic archwire made of stainless steel (304). To begin the electroless plating process there is a need for preparation of the substrate surface. The first step is degreasing by acetone followed by propanol, water rinse and drying under nitrogen flow. The wire is then treated in a plasma asher (March) for 5 min and a pure nickel film (100nm is deposited by e-beam evaporation (Edwards Auto 306).

[0079] A commercial (ENPLATE Ni-425, Enthone Inc.) electroless plating Ni-P solution was used for the present experiments for coating the orthodontic wires (sds Ormco, California. 0.019x0.025 inch rectangular stainless steel arch wires) and the coating seemed to have poor adhesion as tested by a simple scotch bond test. To overcome this problem a thin film of 80-20% nickel-chromium (Ni-Cr) was deposited by e-beam evaporation instead of a pure Ni film. However the electroless reaction could not be initiated on this film. To overcome this difficulty and initiate the electroless plating, a layer of pure Ni was e-beam evaporated on the Ni-Cr film and plating was achieved. The triple layer coating seemed to have adequate adhesion strength tested by scotch-bond and by bending the wire.

[0080] The next step was to add the inorganic fullerene-like nanoparticles of WS_2 (*IF*-WS_2) to the electroless plating solution in order to incorporate it into the Ni-P layer. For that purpose, 200mg of WS_2 were added to 100ml solution and dispersed by a magnetic stirrer. However this process did not result in a stable suspension. The *IF*-nanoparticles quickly agglomerated and precipitated. To suspend the *IF*-nanoparticles in the plating bath, a series of surfactants were tested including Triton-x, sodium dodecylsulfate (SDS) and cetyltrimethylammoniumbromide (CTAB). The CTAB cationic surfactant gave the best results but the amount of the agglomerated nanoparticles was still very high. In order to achieve a more stable suspension, an ultrasonic probe (sonifaier 150, Bramson-30 watts output) was inserted into the solution for one minute. This resulted in an evenly dispersed solution that was stable for long periods of time. Transmission electron microscopy (model CM120, FEI)(TEM) analysis indicated that under these conditions the agglomerates of the IF nanoparticles. could be suspended without damaging the nanoparticles.

[0081] With this resulting solution, SS wires were coated. First, the wires were treated with 20% HF and were inserted in the electroless bath. In this case a coating of Ni-P-*IF*-WS_2 was accomplished. Having a layer of Ni-Cr and/or Ni underneath the Ni-P-*IF*-WS_2 further improved the continuous properties of the coating. The wires were then annealed at 400°C in N_2 atmosphere for one hour and then tested with a ball on flat tester as described above and compared to the uncoated wires.

[0082] To simulate the type of movement, which occurs during orthodontic treatment when the sliding of a tooth across an archwire is preformed, a system described by Redlich et al was utilized [Redlich et al., Am. J. Orthod. Dentofacial Orthop. 124, 69-73 (2003)]. Upper right incisor (0.022x0.028) SS straight wire brackets (GAC, NY) were bonded with cyanoacrylate glue to aluminum plates by a bracket-mounting apparatus (**Figs. 10**)). This apparatus insures the accurate and similar positioning of the brackets on the plates. These plates were then connected to the base of an INSTRON 4502 testing machine through a device with 3 different notches angulated at 0°, 5° and 10° to the long axis of the device (**Fig. 11**). Angulations represent the contact angle between the wire and bracket during the movement of the tooth. 12-cm segments of the orthodontic wires (coated & uncoated) were attached, on their upper part, to a 10 Newton load cell and the lower end was connected to a 150g weight. The wires were then inserted into the slots in the brackets and ligated with an elastomeric module (Sani-Ties Silvar, GAC) to all 4 wings of the brackets (**Fig. 12**).

[0083] In this setup the Instron was set to move the bracket down along the wire at a constant speed of 10 mm/min to a distance of 5 mm. The test begins with a steady increase in the force and reaches a maximum when movement begins on the wire. This maximum represents the static friction and is the force that is of interest in this case.

[0084] Uncoated and coated wires were tested at the 3 different angles. The first tests on the coated wires resulted in high friction levels that were overcome by a run-in period of repeated back and forth movements of the wire in the bracket. At the highest angle (10°) the tests were further conducted in a wet mode with DI water dripping on the bracket and wire during the test simulating the saliva in the interface when the movement occurs in the mouth. The tests were repeated 5 times for each group and all the data was recorded onto the operating system of the INSTRON and then analyzed and plotted.

BIOCOMPATIBILITY TESTS AND RESULTS

[0085] Toxicology tests of the *IF*-WS_2 reported the material as being non-toxic in an oral administration in rats. The presence of Ni in orthodontic appliances is known and they are approved for use (except in people with an allergic sensitivity to Ni).

EXPERIMENTAL DESIGN CONDITIONS:

REPLACE TABLE - NOT CLEAR

1. Constitution of Test Groups and Dose Levels:

[0086]

Group No. & General (d)	Group Size (d)	Individual Animal No.'s	TREATMENT			
			Test Compound	Route	Dose (mg/kg)	Volume Dosage (ml/kg)
1F	n=6	1,2,3,4,5,6	*Inorganic fullerene-like WS_2*	PO	300	5ml/kg
2F	n=6	7,8,9,10,11,12	*nanospheres (IF-WS_2)*		2000	

2. Principles of the Test:

[0087]

Due to the lack of information regarding potential toxicity, and in accordance with the Guideline recommendation, the sequential method applied in this study represents a stepwise procedure, using a minimum amount of animals. Dosing was sequential and the time interval between the test groups dosing was determined by the lack of adverse effects following dosing.

3. Administration:

3.1 Route of Administration:

[0088] All animals were subjected to a single oral gavage (PO) administration.

3.2 Dose Levels:

[0089] The Test Item as supplied by the Sponsor was administered at two dose levels of 300 and 2000 mg/kg.

3.3 Volume Dosage:

[0090] In all instances the volume dosage was 5 ml/kg.

4. Justification for Route of Administration and Dose Levels:

[0091] The oral route was chosen as the route of administration since in order to assess the toxic characteristics of substances the determination of acute oral toxicity is usually an initial step. The initial dose level selected was based on the Sponsor's specific request and according to the respective guideline.

5. Observations and Examinations:

5.1 Clinical Signs:

[0092] Animals were observed continuously during the first 7-8 hours following dosing and then periodically during the first 24 hours. Clinical signs were recorded. Animals were observed for a total during of 14 days. Observations included that of the skin, fur, eyes, mucous membranes, occurrence of secretions and excretions (e.g. diarrhea) and autonomic activity (e.g. lacrimation, salivation, piloerection, pupil size, unusual respiratory pattern). Additional items that were observed were the gait, posture and response to handling, as well monitoring for any presence of bizarre behavior, tremors, convulsions, sleep and coma.

5.2 Body Weight:

[0093] Determination of individual body weights of animals was made shortly before Test Item administration, 2 and 7 days following dosing and at the end of the study prior to the scheduled necropsy.

6. Necropsy Procedures and Macroscopic Examination:

[0094] All test animals were subjected to full detailed macroscopic necropsy. All gross pathological changes were recorded for each animal.

DATA EVALUATION:

[0095] Evaluation included monitoring the relationship, if any, between the animals' exposure to the Test Item and the incidence and severity of all abnormalities including: effects on mortality, behavioral and clinical abnormalities, body weight changes, gross lesions, and any other toxic effects.

ANIMAL CARE AND USE STATEMENT:

RESULTS:

[0096]

1. **Mortality** (Table 1):

   No mortality occurred in any of the animals throughout the entire 14-day observation period.

2. **Clinical Signs** (Table 2):

No noticeable clinical signs in reaction to dosing were evident in any of the animals administered with Inorganic fullerene-like WS_2 nanospheres (*IF*=WS_2) at the immediate post-dosing period or during the entire 14-day observation period.

3. Body Weight (Table 3-5):

Body weight gain of all animals was found to be within range of normally expected values.

4. Macroscopic Examination: (Table 6):

No pathological changes were observed in any of the animals during necropsy procedure.

CONCLUSION:

[0097] In consideration of the lack of mortality at dose levels of 300 and 2000 mg/kg PO (oral administration), the Test Item Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* is allocated to "Category 5" or "Unclassified" in accordance with the classification by GHS (Globally Harmonized System) (e).

Table 1: Mortality Incidence Observed throughout the Entire 14-day Observation Period, in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (Batch No.: HP6):

Group No. & Gender	Group Size	Test Material	MORTALITY (Number affected / Total number of animals)
1F	*n=6*	Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (300 mg/kg)	0/6
2F	*n=6*	Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	0/6

Table 2: Individual Clinical Signs Observed throughout the Entire 14-day Observation Period, in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2):*

Group No. & Gender	Individual Animal No.	Test Material	OBSERVATION (Number affected / Total number of animals Day of Dosing (Day 0)	Day 1-13
1F	1	Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (300 mg/kg)	NAD	NAD
	2		NAD	NAD
	3		NAD	NAD
	4		NAD	NAD
	5		NAD	NAD
	6		NAD	NAD
2F	7	Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	NAD	NAD
	8		NAD	NAD
	9		NAD	NAD
	10		NAD	NAD
	11		NAD	NAD
	12		NAD	NAD

NAD = No Abnormality Detected

Table 3: Individual and Mean (± SD) Group Values of body Weights in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)*:

Group No. & Gender	Test Material	Individual Animal No.	Body Weight (g) Day 0	Day 2	Day 7	Day 14
1F	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (300mg/kg)	1	177	194	209	228
		2	183	203	225	233
		3	173	192	205	222
		4	185	202	213	231
		5	182	196	207	225
		6	186	209	213	228
		Mean	**181**	**199**	**212**	**228**
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±*SD*	*5.0*	*6.4*	*7.1*	*4.0*
2F	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	7	190	207	212	223
		8	194	206	211	223
		9	209	217	228	238
		10	195	208	222	235
		11	195	213	222	233
		12	199	214	228	231
		Mean	**197**	**211**	**221**	**231**
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±*SD*	6.5	*4.4*	*7.5*	*5.3*

Table 4: Individual and Mean (±SD) Group Values of **Body Weight Gain** (g) in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (Batch No.: HP6):

Group No. & Gender	Test Material	Individual Animal No.	Body Weight (g) Day 0-2	Day 2-7	Day 7-14	Day 0-14
1F	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (300 mg/kg)	1	17	15	19	51
		2	20	22	8	50
		3	19	13	17	49
		4	17	11	18	46
		5	14	11	18	43
		6	23	4	15	42
		Mean	**18**	**13**	**16**	**47**
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±*SD*	*3.1*	*5.9*	*4.1*	*3.8*

(continued)

Group No. & Gender	Test Material	Individual Animal No.	Body Weight (g) Day 0-2	Day 2-7	Day 7-14	Day 0-14
	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	7	17	5	11	33
		8	12	5	12	29
		9	8	11	10	29
		10	13	14	13	40
		11	18	9	11	38
		12	13	14	3	32
		Mean	**14**	**10**	**10**	**34**
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±SD	*3.7*	*4.1*	*3.6*	*4.6*

Table 5: Individual and Mean (±SD) Group Values of **Percentage (%) Body Weight Gain** in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (Batch No.: HP6):

Group No. & Gender	Test Material	Individual Animal No.	Body Weight (g) Day 0-2	Day 2-7	Day 7-14	Day 0-14
1F	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (300 mg/kg)	1	9.6	7.7	9.1	28.8
		2	10.9	10.8	3.6	27.3
		3	11.0	6.8	8.3	28.3
		4	9.2	5.4	8.5	24.9
		5	7.7	5.6	8.7	23.6
		6	12.4	1.9	7.0	22.6
		Mean	**10**	**6**	**8**	**26**
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±SD	*1.6*	*2.9*	*2.1*	*2.6*
2F	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	7	8.9	2.4	5.2	17.4
		8	6.2	2.4	5.7	14.9
		9	3.8	5.1	4.4	13.9
		10	6.7	6.7	5.9	20.5
		11	9.2	4.2	5.0	19.5
		12	7.5	6.5	1.3	16.1
		Mean	7	5	5	17
			(n=6)	*(n=6)*	*(n=6)*	*(n=6)*
		±SD	*2.0*	*1.9*	*1.7*	*2.6*

Table 6: Individual Gross Necropsy Findings in Female Sprague-Dawley™ Rats, Following a Single Oral Administration of Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2)* (Batch No.: HP6):

Group No.	TREATMENT	Animal No.	OBSERVATION
	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (300 mg/kg)	1	NAD
		2	NAD
		3	NAD
		4	NAD
		5	NAD
		6	NAD
	Inorganic-fullerene-like WS_2 nanospheres *(IF-WS_2)* (2000 mg/kg)	7	NAD
		8	NAD
		9	NAD
		10	NAD
		11	NAD
		12	NAD

SUMMARY:

[0098]

1. The potential acute toxicity of the Test Item Inorganic fullerene-like WS_2 nanospheres *(IF-WS_2) (**Batch No. HP6**)* was assessed on the basis of the testing procedure recommended by OECD Guideline for the Testing of Chemicals, Section 4, No. 423, "Acute Oral Toxicity - Acute Toxic Class Method", adopted December 17th, 20001.

2. **Inorganic fulerene-like WS_2 nanospheres (*IF*-WS_2) *(Batch No. HP6)*** was administered successively to two groups of *n=6* female Sprague-Dawley™ (SD™) rats per each dose levels of 300 and 2000 mg/kg.

3. Animals were observed for a total duration of 14 days following dosing.

4. Body weight gain of all animals was found to be within range of normally expected values [b].

5. No mortality occurred in any of the animals throughout the entire 14-day study period.

6. No adverse signs in reaction to treatment were evident in any of the animals during the immediate post-dosing times or throughout the entire 14-day observation period.

7. No gross pathological findings were noted in any of the animals by necropsy inspection.

8. In consideration of the lack of mortality at dose levels of 300 and 2000 mg/kg PO (oral administration), the Test Item Inorganic fullerene-like WS_2 nanospheres (*IF*-**WS_2**) ***(Batch No. HP6)*** is allocated to "Category 5" or "Unclassified" in accordance with the classification by GHS (Globally Harmonized System)[c].

Claims

1. A biocompatible medical or dental article, the article being elongated and coated at least partially by (i) inorganic fullerene-like *(IF)* nanoparticles or (ii) a composite containing such nanoparticles.

2. An article according to claim 1, being in a form of wire or tube.

3. An article according to claim 1 or 2 being circular or rectangular in cross-section.

4. An article according to any one of claims 1-2, wherein the IF-nanoparticles are self-lubricating.

5. An article according to any one of claims 1-4, wherein said composite is selected from Ni-P-*IF*-nanoparticles, Co-P-*IF*-nanoparticles, Co-B-*IF*-nanoparticles, Ni-B-*IF*-nanoparticles, metal film containing *IF*-nanoparticles, polyurethane, polypropylene or epoxy containing *IF*-nanoparticles or a sol-gel glass containing *IF*-nanoparticles.

6. An article according to any one of claims 1-5, wherein said *IF* nanoparticles are made of metal chalcogenide or metal dichalcogenide.

7. An article according to claim 1-5, wherein said *IF* nanoparticles are made of TiS_2, $TiSe_2$, $TiTe_2$, WS_2, WSe_2, WTe_2, MoS_2, $MoSe_2$, $MoTe_2$, SnS_2, $SnSe_2$, $SnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, GaS, GaSe, GaTe, InS, InSe, HfS_2, ZrS_2, VS_2, ReS_2 or NbS_2.

8. An article according to claim 5, wherein said composite comprises (i) Ni-P, Co-P, Co-B or Ni-B, and (ii) *IF*-WS_2 or *IF*-MoS_2 nanoparticles.

9. An article according to claim 5, wherein said *IF*-nanoparticles are *IF*-WS_2 or *IF*-MoS_2 nanoparticles.

10. An article according to any one of claims 1-9, wherein said coating is biocompatible.

11. An article according to any one of claims 1-10, wherein said coating has a thickness of between 0.3 micron and 50 microns.

12. An article according to claim 11, wherein said coating has a thickness of between 1 micron and 10 microns.

13. An article according to any one of claims 1-12 selected from dental implant, orthodontic wire, orthodontic archwire, orthodontic bracket, band, bonded or banded orthodontic attachment, palatal expanders, screw-type dental implant, mobile functioning native or artificial human joint, hip replacement, tissue-penetrating device, feeding oral and nasal tubes used for laparoscopic surgery, a needle, and a catheter.

14. An article according to any one of claims 1-13, made of metal, rubber, glass or plastic.

15. Method of coating an elongated article with a friction reducing film, to produce the biocompatible medical or dental article of claim 1, the method comprising:

(i) exposing said elongated article to a surface pre-treatment procedure;
(ii) dispersing *IF* nanoparticles within a plating solution to obtain *IF* nanoparticles homogeneously dispersed in said plating solution; and
(iii) contacting the article with said plating solution and depositing said nanoparticles on one or more surfaces of said article through electroless or electrochemical deposition, thereby obtaining an article coated on at least part of its surfaces with a friction reducing film comprising *IF* nanoparticles or composite containing such nanoparticles.

16. Method according claim 15, wherein the surface pre-treatment procedure is carried out with an etching acidic solution.

17. Method according to claim 16, wherein said acidic solution is HF.

18. Method according to any one of claims 15-17, comprising one or more additional deposition steps prior to said contacting to form intermediate layers between the article and the outer, friction-reducing film.

19. Method according to any one of claims 15-18, wherein said article is made of metal and said coating comprises a friction reducing film comprising composite of Ni-P, Co-B, Ni-B or Co-P and *IF* nanoparticles.

20. Method according to any one of claims 15-19, wherein said friction reducing film has a thickness of between 0.3 micron and 50 microns.

Patentansprüche

1. Biokompatibler medizinischer oder zahnärztlicher Artikel, wobei der Artikel länglich ist und mindestens teilweise mit (i) anorganischen Fulleren-artigen (*IF*) Nanopartikeln oder (ii) einem Verbundmaterial, das solche Nanopartikel enthält, beschichtet ist.

2. Artikel nach Anspruch 1, die Form eines Drahts oder Rohrs aufweisend.

3. Artikel nach Anspruch 1 oder 2, einen kreisförmigen oder rechteckigen Querschnitt aufweisend.

4. Artikel nach einem der Ansprüche 1 bis 2, wobei die IF-Nanopartikel selbstschmierend sind.

5. Artikel nach einem der Ansprüche 1 bis 4, wobei das Verbundmaterial aus Ni-P-*IF*-Nanopartikeln, Co-P-*IF*-Nanopartikeln, Co-B-*IF*-Nanopartikeln, Ni-B-*IF*-Nanopartikeln, IF-Nanopartikel enthaltendem Metallfilm, Nanopartikel enthaltendem Polyurethan, Polypropylen oder Epoxidharz oder einem *IF*-Nanopartikel enthaltenden Sol-Gel-Glas ausgewählt ist.

6. Artikel nach einem der Ansprüche 1 bis 5, wobei die *IF*-Nanopartikel aus Metallchalkogenid oder Metalldichalkogenid hergestellt sind.

7. Artikel nach einem der Ansprüche 1 bis 5, wobei die *IF*-Nanopartikel aus TiS_2, TiSe2, TiTe2, WS_2, WSe_2, WTe_2, MoS_2, $MoSe_2$, $MoTe_2$, SnS_2, $SnSe_2$, $SnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, GaS, GaSe, GaTe, InS, InSe, HfS_2, ZrS_2, VS_2, ReS_2 oder NbS_2 hergestellt sind.

8. Artikel nach Anspruch 5, wobei das Verbundmaterial (i) Ni-P-, Co-P-, Co-B- oder Ni-B-, und (ii) *IF*-WS_2- oder *IF*-MoS_2-Nanopartikel umfasst.

9. Artikel nach Anspruch 5, wobei die *IF*-Nanopartikel IF-WS_2-oder *IF*-MoS_2-Nanopartikel sind.

10. Artikel nach einem der Ansprüche 1 bis 9, wobei die Beschichtung biokompatibel ist.

11. Artikel nach einem der Ansprüche 1 bis 10, wobei die Beschichtung eine Dicke zwischen 0,3 Mikrometer und 50 Mikrometer aufweist.

12. Artikel nach Anspruch 11, wobei die Beschichtung eine Dicke zwischen 1 Mikrometer und 10 Mikrometer aufweist.

13. Artikel nach einem der Ansprüche 1 bis 12, ausgewählt aus einem Dentalimplantat, einem orthodontischen Draht, einem orthodontischen Bogendraht, einer orthodontischen Klammer, einem Band, einer geklebten oder gebänderten orthodontischen Befestigung, einem palatinalen Expander, einem Schrauben-Dentalimplantat, einem mobil funktionierenden nativen oder künstlichen menschlichen Gelenk, einer Hüftprothese, einer gewebedurchdringenden Vorrichtung, oralen und nasalen Zuführschläuchen für laparoskopische Chirurgie, einer Nadel und einem Katheter.

14. Artikel nach einem der Ansprüche 1 bis 13, hergestellt aus Metall, Gummi, Glas oder Kunststoff.

15. Verfahren zum Beschichten eines länglichen Artikels mit einem reibungsvermindernden Film zur Herstellung des biokompatiblen medizinischen oder zahnärztlichen Artikels nach Anspruch 1, wobei das Verfahren Folgendes umfasst:

    (i) Aussetzen des länglichen Artikels einem Oberflächenvorbehandlungsverfahren;
    (ii) Dispergieren von *IF*-Nanopartikeln in einer Plattierungslösung, um homogen in der Plattierungslösung dispergiert *IF*-Nanopartikel zu erhalten; und
    (iii) Inkontaktbringen des Artikels mit der Plattierungslösung und Abscheiden der Nanopartikel auf einer oder mehreren Oberflächen des Artikels durch stromlose oder elektrochemische Abscheidung, wodurch ein Artikel erhalten wird, der auf mindestens einem Teil seiner Oberflächen mit einem reibungsvermindernden Film beschichtet ist, der *IF*-Nanopartikel oder ein Verbundmaterial, das solche Nanopartikel enthält, umfasst.

16. Verfahren nach Anspruch 15, wobei das Oberflächenvorbehandlungsverfahren mit einer ätzenden, sauren Lösung durchgeführt wird.

17. Verfahren nach Anspruch 16, wobei die saure Lösung HF ist.

18. Verfahren nach einem der Ansprüche 15-17, umfassend einen oder mehrere zusätzliche Abscheidungsschritte zur Bildung von Zwischenschichten zwischen dem Artikel und der äußeren, reibungsvermindernden Folie vor dem Inkontaktbringen.

19. Verfahren nach einem der Ansprüche 15-18, wobei der Artikel aus Metall hergestellt ist und die Beschichtung einen reibungsvermindernden Film umfasst, der ein Verbundmaterial aus Ni-P-, Co-B-, Ni-B- oder Co-P- und *IF*-Nanopartikel umfasst.

20. Verfahren nach einem der Ansprüche 15-19, wobei der reibungsverringernde Film eine Dicke zwischen 0,3 Mikrometer und 50 Mikrometer aufweist.

Revendications

1. Article médical ou dentaire biocompatible, l'article étant allongé et revêtu au moins partiellement (i) de nanoparticules inorganiques de type fullerène *(IF)* ou (ii) d'un composite contenant de telles nanoparticules.

2. Article selon la revendication 1, étant sous forme de fil ou de tube.

3. Article selon la revendication 1 ou 2, étant de coupe transversale circulaire ou rectangulaire.

4. Article selon l'une quelconque des revendications 1 à 2, dans lequel les nanoparticules *IF* sont autolubrifiantes.

5. Article selon l'une quelconque des revendications 1 à 4, dans lequel ledit composite est choisi parmi Ni-P-nanoparticules *IF,* Co-P-nanoparticules *IF,* Co-B-nanoparticules *IF,* Ni-B-nanoparticules *IF,* un film en métal contenant des nanoparticules *IF*, du polyuréthane, polypropylène ou époxy contenant des nanoparticules *IF* ou un verre sol-gel contenant des nanoparticules *IF*.

6. Article selon l'une quelconque des revendications 1 à 5, dans lequel lesdites nanoparticules *IF* sont constituées de chalcogénure de métal ou de dichalcogénure de métal.

7. Article selon la revendication 1 à 5, dans lequel lesdites nanoparticules *IF* sont constituées de TiS_2, $TiSe_2$, $TiTe_2$, WS_2, WSe_2, WTe_2, MoS_2, $MoSe_2$, $MoTe_2$, SnS_2, $SnSe_2$, $SnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, GaS, GaSe, GaTe, InS, InSe, HfS_2, ZrS_2, VS_2, ReS_2 ou NbS_2.

8. Article selon la revendication 5, dans lequel ledit composite comprend (i) Ni-P, Co-P, Co-B or Ni-B, et (ii) des nanoparticules *IF*-WS_2 ou *IF*-MoS_2.

9. Article selon *l*a revendication 5, dans lequel lesdites nanoparticules *IF* sont des nanoparticules *IF*-WS_2 ou *IF*-MoS_2.

10. Article selon l'une quelconque des revendications 1 à 9, dans lequel ledit revêtement est biocompatible.

11. Article selon l'une quelconque des revendications 1 à 10, dans lequel ledit revêtement a une épaisseur comprise entre 0,3 micron et 50 microns.

12. Article selon la revendication 11, dans lequel ledit revêtement a une épaisseur comprise entre 1 micron et 10 microns.

13. Article selon l'une quelconque des revendications 1 à 12, choisi parmi un implant dentaire, un fil orthodontique, un arc dentaire orthodontique, un bracket orthodontique, une bague, une fixation orthodontique collée ou baguée, des extenseurs palataux, un implant dentaire de type vis, une articulation humaine native ou artificielle fonctionnelle mobile, une prothèse de hanche, un dispositif de pénétration de tissu, des tubes d'alimentation oraux et nasaux utilisés pour la chirurgie laparoscopique, une aiguille et un cathéter.

14. Article selon l'une quelconque des revendications 1 à 13, constitué de métal, caoutchouc, verre ou plastique.

15. Procédé de revêtement d'un article allongé avec un film de réduction de frottement, pour produire l'article médical ou dentaire biocompatible selon la revendication 1, le procédé comprenant :

(i) l'exposition dudit article allongé à une procédure de prétraitement de surface ;
(ii) la dispersion de nanoparticules *IF* au sein d'une solution de placage de façon à obtenir des nanoparticules *IF* homogènement dispersées dans ladite solution de placage ; et
(iii) la mise en contact de l'article avec ladite solution de placage et le dépôt desdites nanoparticules sur une ou plusieurs surfaces dudit article par le biais d'un dépôt autocatalytique ou électrochimique, ce qui permet d'obtenir un article revêtu sur au moins une partie de ses surfaces d'un film de réduction de frottement comprenant des nanoparticules *IF* ou un composite contenant de telles nanoparticules.

16. Procédé selon la revendication 15, dans lequel la procédure de prétraitement de surface est effectuée avec une solution acide d'attaque chimique.

17. Procédé selon la revendication 16, dans lequel ladite solution acide est HF.

18. Procédé selon l'une quelconque des revendications 15 à 17, comprenant une ou plusieurs étapes de dépôt supplémentaires avant ladite mise en contact pour former des couches intermédiaires entre l'article et le film externe de réduction de frottement.

19. Procédé selon l'une quelconque des revendications 15 à 18, dans lequel ledit article est constitué de métal et ledit revêtement comprend un film de réduction de frottement comprenant un composite de Ni-P, Co-B, Ni-B ou Co-P et de nanoparticules IF.

20. Procédé selon l'une quelconque des revendications 15 à 19, dans lequel ledit film de réduction de frottement a une épaisseur comprise entre 0,3 micron et 50 microns.

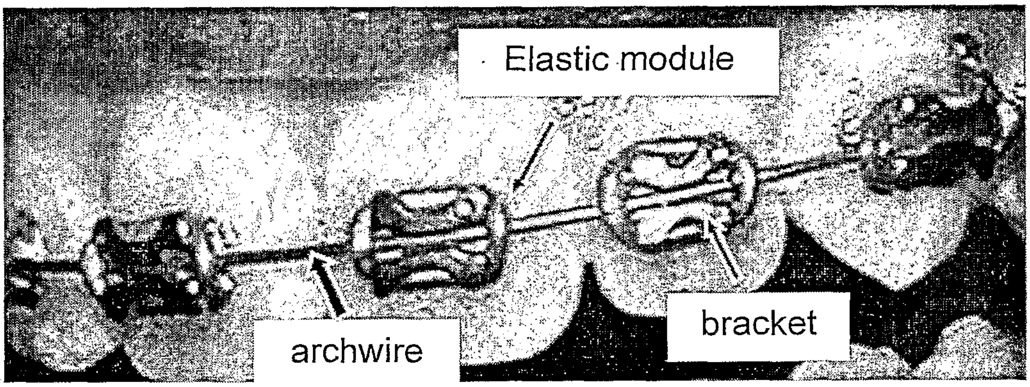

FIG. 1

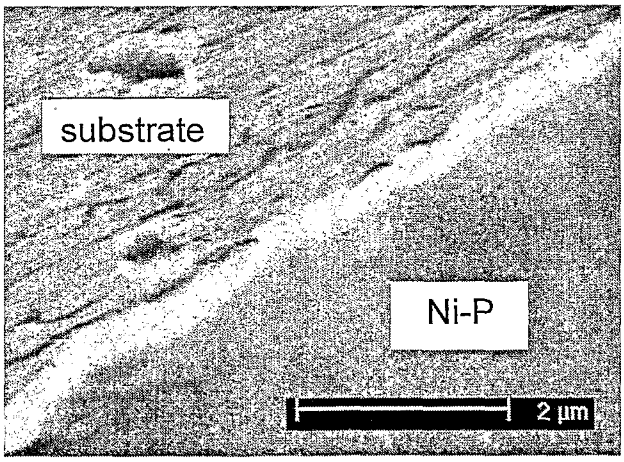

FIG. 2

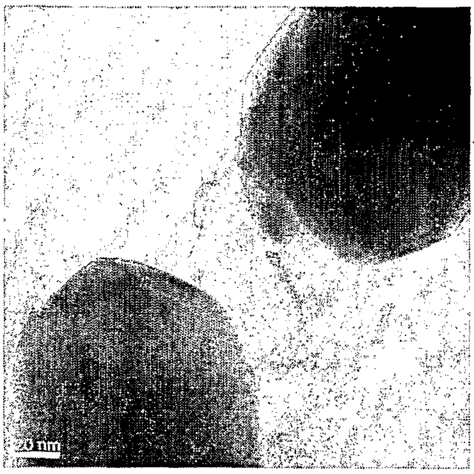

FIG. 3A

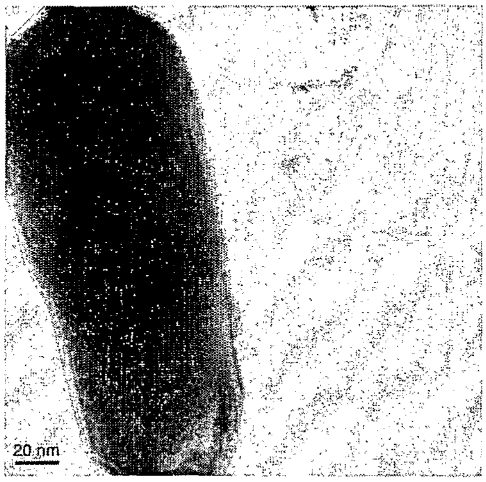

FIG. 3B

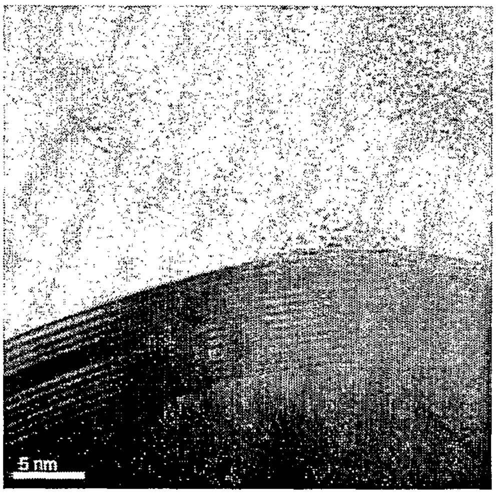

FIG. 3C

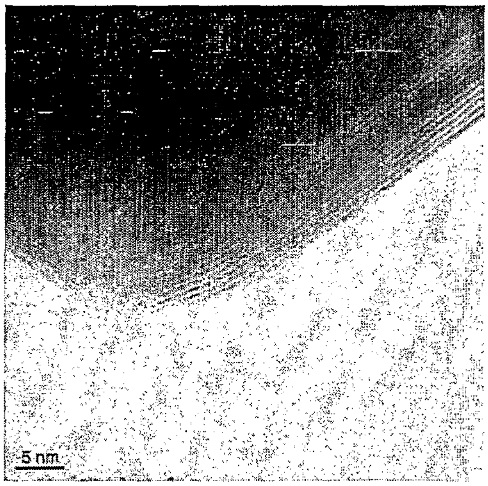

FIG. 3D

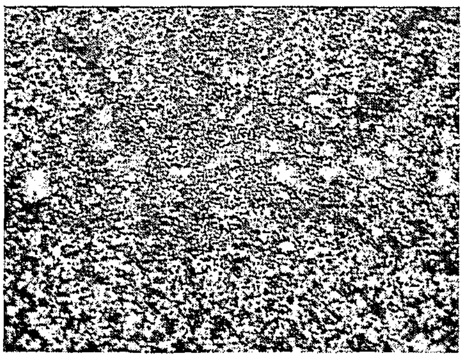

FIG. 4

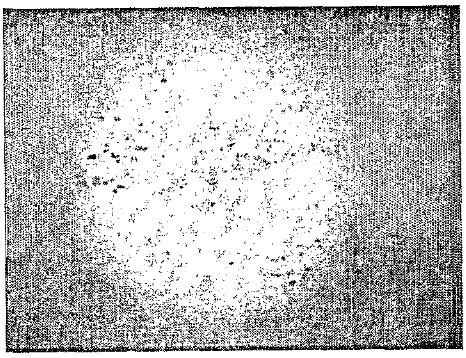

FIG. 5A

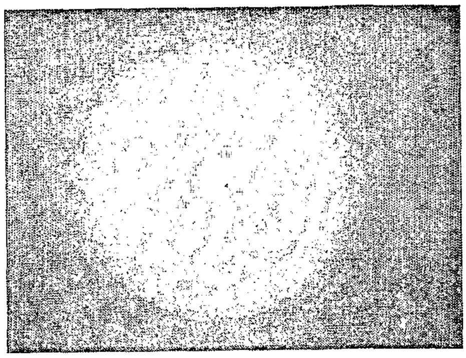

FIG. 5B

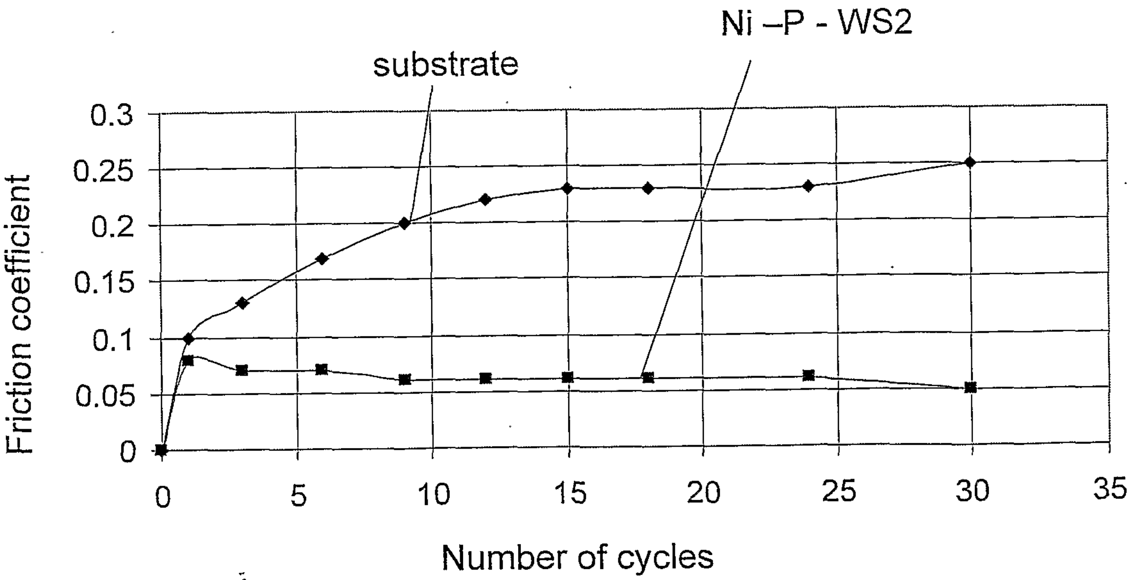

FIG. 6

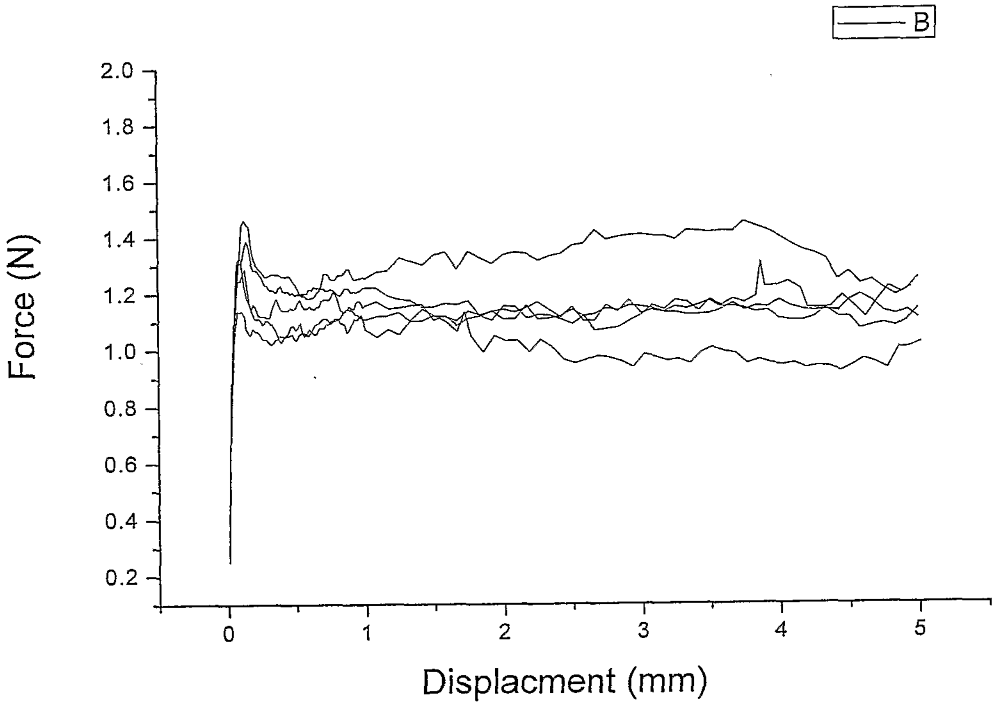
B
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 7A

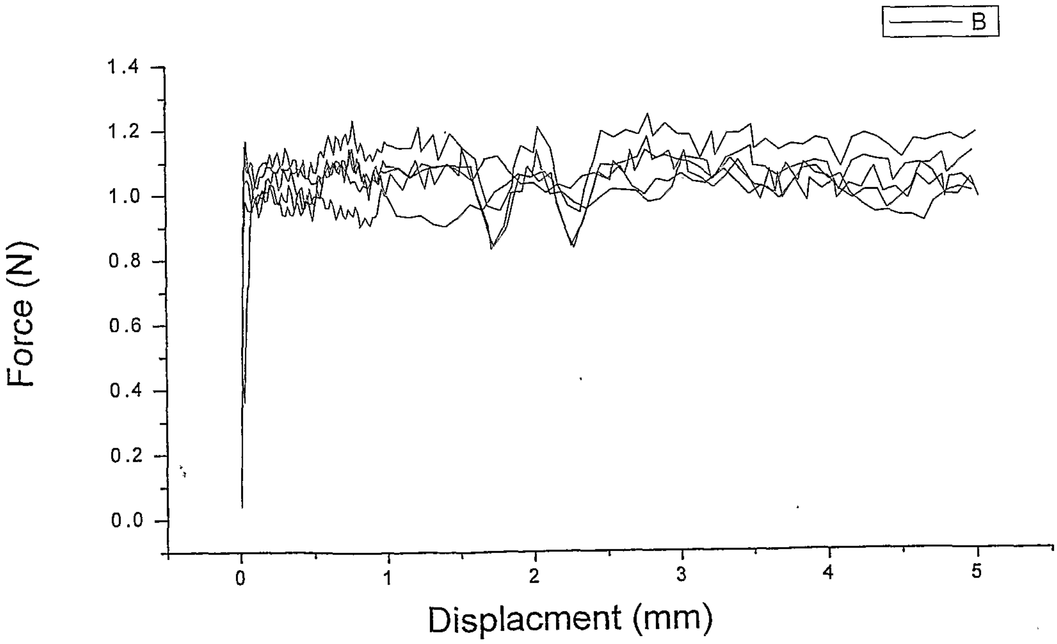
B
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 7B

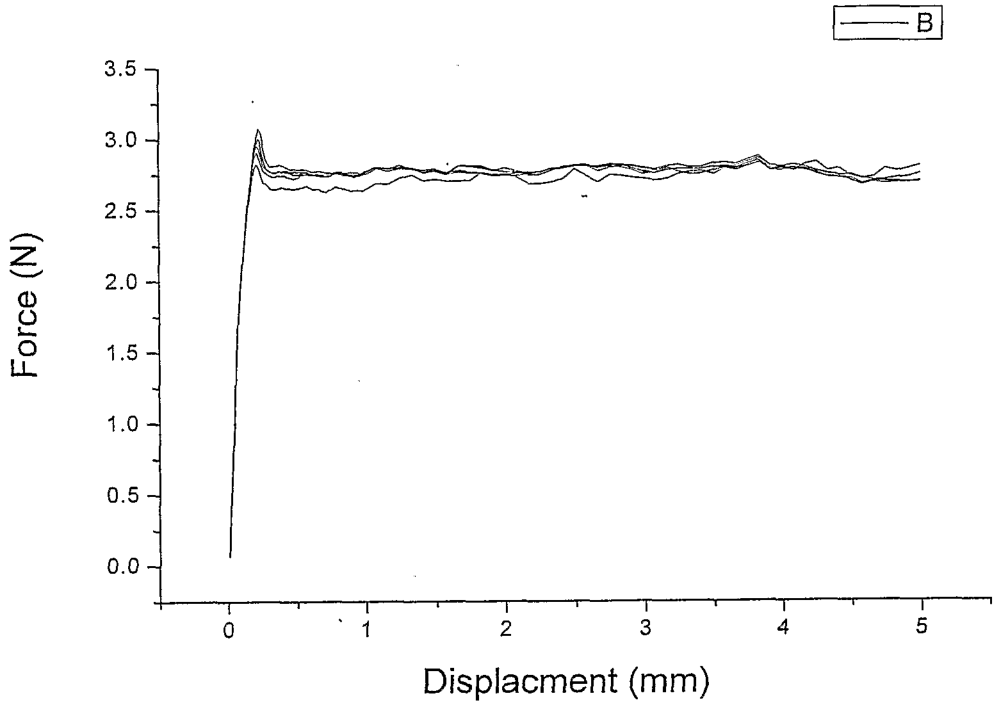
B
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 8A

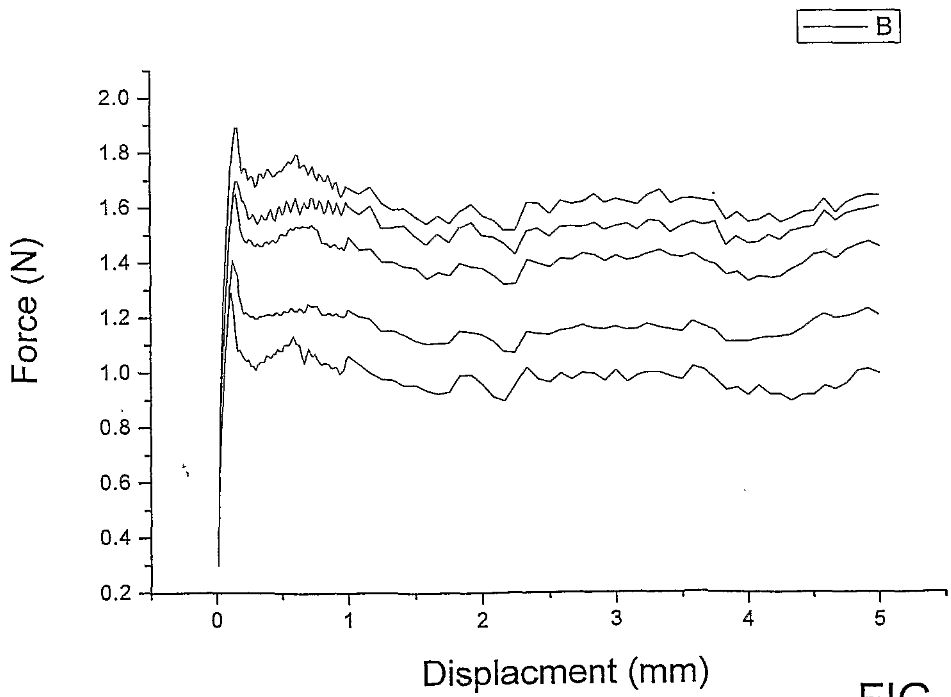
B
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 8B

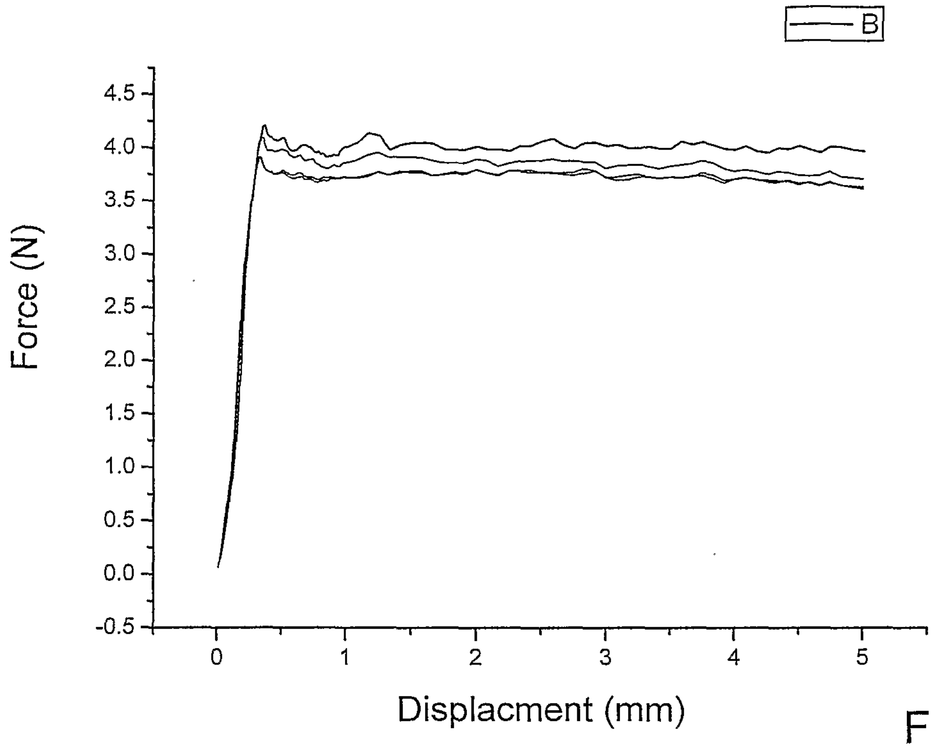
B
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 9A

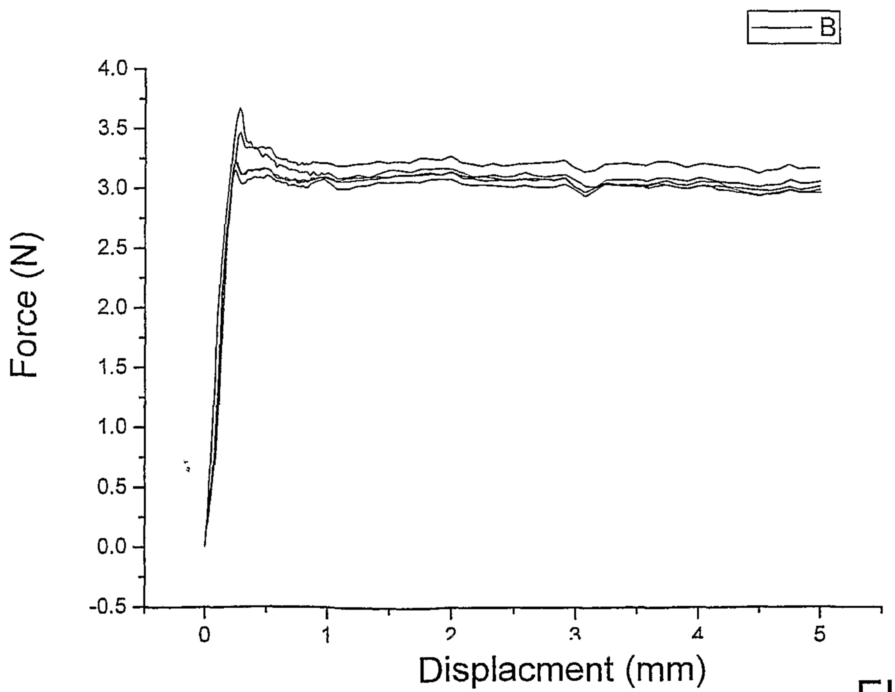
B
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
Force (N)
0
1
2
3
4
5
Displacment (mm)

FIG. 9B

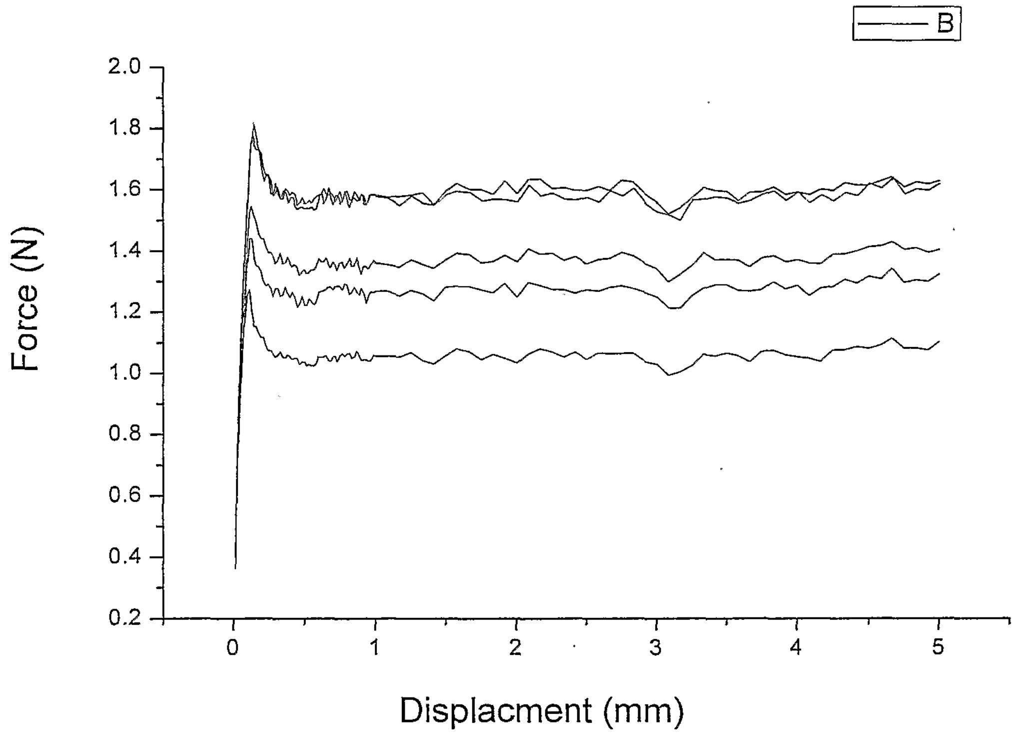

FIG. 9C

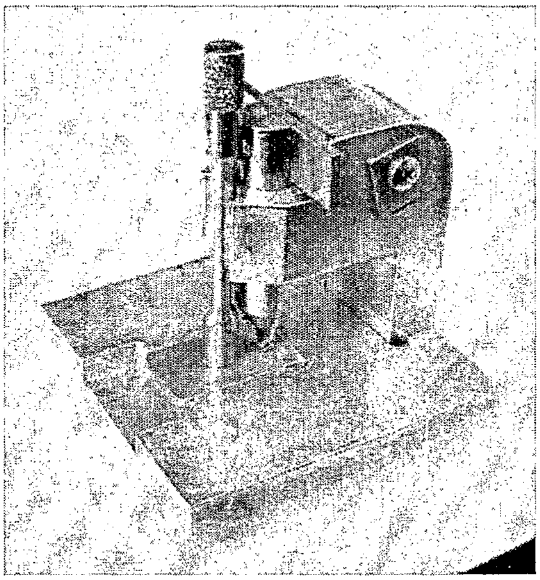

FIG. 10

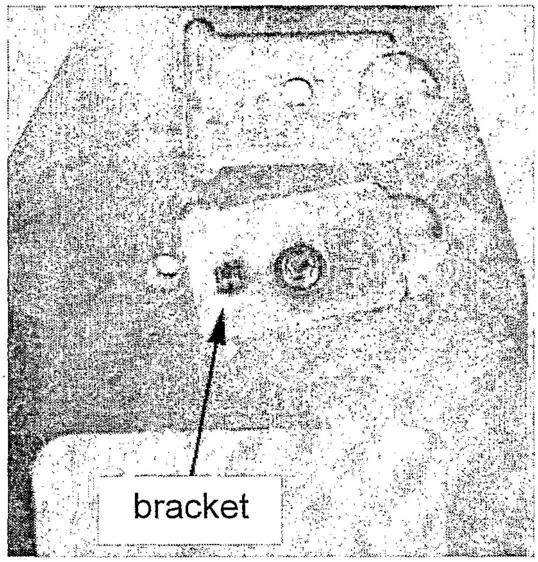

FIG. 11

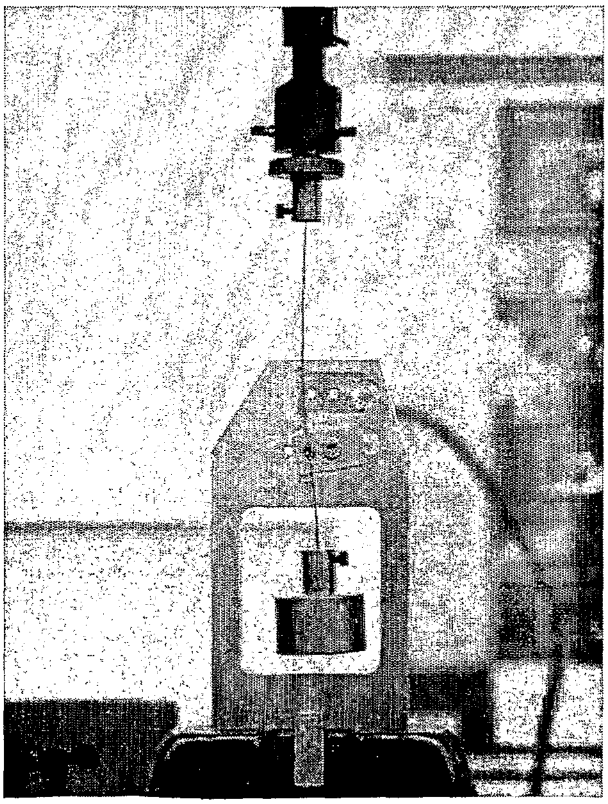

FIG. 12

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5288230 A **[0002] [0009]**
- US 5454716 A **[0002] [0009]**
- US 5958358 A **[0002] [0024]**
- US 6299438 B **[0002] [0009]**
- US 20030144155 A1 **[0003]**

Non-patent literature cited in the description

- **CHEN et al.** *Adv. Eng. Mat.,* 2002, vol. 4 (9), 686-690 **[0002] [0052]**
- **L. RAPOPORT et al.** *Wear,* 2003, vol. 255, 785-793 **[0002] [0025]**
- **REDLICH et al.** *Am. J. Orthod. Dentofacial Orthop.,* 2003, vol. 124, 69-73 **[0002] [0082]**
- **TENNE R. et al.** *Nature,* 1992, vol. 360, 444-445 **[0002] [0024]**
- Wear and Friction of Ni-P Electroless Composite Coating Including Inorganic Fullerene-WS2Nanoparticles. *Advanced Ingineering Material,* 2002 **[0003]**
- **RAPOPORT et al.** *Wear,* 2003, vol. 255, 785-793 **[0072]**
- OECD Guideline for the Testing of Chemicals. *Acute Oral Toxicity - Acute Toxic Class Method* **[0098]**

patsnap

专利名称(译)	低摩擦涂层，用于牙科和医疗设备		
公开(公告)号	EP1885249A4	公开(公告)日	2012-12-26
申请号	EP2006745103	申请日	2006-05-17
[标]申请(专利权)人(译)	耶达研究及发展有限公司 HOLON学术INST高科技		
申请(专利权)人(译)	烟台开发区研究开发有限责任公司. HADASIT医学研究服务和发展COMPANY LTD. HOLON学术理工大学		
当前申请(专利权)人(译)	烟台开发区研究开发有限责任公司. HADASIT医学研究服务和发展COMPANY LTD. HOLON学术理工大学		
[标]发明人	TENNE RESHEF KATZ ALON REDLICH MEIR RAPOPORT LEV		
发明人	TENNE, RESHEF KATZ, ALON REDLICH, MEIR RAPOPORT, LEV		
IPC分类号	A61B8/14 A61C3/00 A61C5/77 B21F43/00		
CPC分类号	A61C7/20 A61C7/14 A61C8/0013 A61L27/303 A61L29/103 A61L31/084 C23C18/165 C23C18/1662 C23C18/32 C25D3/562 C25D5/34 C25D15/02 Y10T428/13 Y10T428/264 Y10T428/31511 Y10T428/31609 Y10T428/31678 Y10T428/31855		
优先权	60/681443 2005-05-17 US		
其他公开文献	EP1885249A2 EP1885249B1		
外部链接	Espacenet		

摘要(译)

本发明提供一种制品，其至少一部分被无机类富勒烯（IF）纳米颗粒或含有这种纳米颗粒的复合物涂覆。优选地，本发明提供由金属制成的制品，用于牙科或医学，例如，弓丝，针或导管，具有减小摩擦的薄膜，以及用减摩膜涂覆这种制品的方法。