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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

(54) Title: METHOD OF COATING POLYXYLYLENE ONTO FLOUROPOLYMER SURFACES AND DEVICES COATED THEREBY

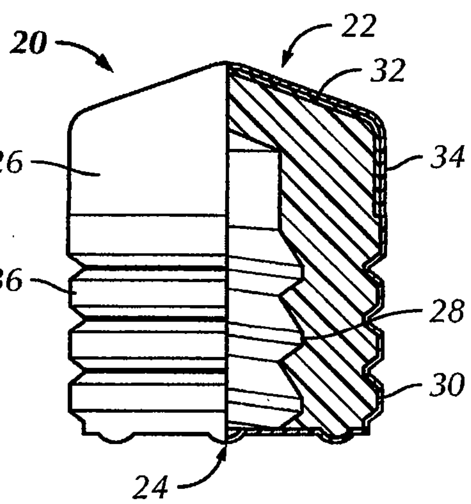

FIG. 4

(57) Abstract: A method relates to coating an elastomeric substrate having a fluoropolymer surface with polyxylylene. The polyxylylene can be applied to the elastomeric component and fluoropolymer surface by chemical or physical vapor deposition. The elastomeric substrate can be at least partially laminated with a fluoropolymer film that is etched before or after lamination with the elastomeric substrate. Alternatively, the elastomeric substrate can be at least partially formed from a fluoropolymer and then etched before being coated with polyxylylene.

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

TITLE OF THE INVENTION

[0001] Method of Coating Polyxylylene onto Fluoropolymer Surfaces and Devices Coated Thereby

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a method of coating fluoropolymer surfaces with polyxylylene. More particularly, the present invention relates to a method of coating fluoropolymer surfaces and devices having a fluoropolymer surface with polyxylylene.

[0003] It is commonly known that fluoropolymers are durable thermoplastic substances that are highly resistant to chemicals, oxidation and UV radiation, are very non-reactive, and have low coefficients of friction. The most widely known fluoropolymer is polytetrafluoroethylene, such as Teflon® by duPont de Nemours & Co., which is readily used for making a variety of non-stick products. Because of these fluoropolymer properties, such materials are difficult to bond to other polymer materials with sufficient adhesive strength without the need for an intervening adhesive layer.

[0004] Polyxylylenes generally have a low coefficient of friction, superior barrier and physical properties, and are moisture resistant. U.S. Patent No. 4,882,210 discloses the use of polyparaxylylene coatings on glass containers to increase the crush strength of the glass container. U.S. Patent Nos. 4,808,453; 4,973,504; and 5,000,994 disclose coating elastomeric closures for pharmaceutical containers with a continuous polyparaxylylene coating of about 0.5 to about 2 microns thickness to reduce the coefficient of friction of the closure and to prevent metal ion extraction from the elastomeric closure. However, none of these patents discloses or relates to the use of polyxylylenes on fluoropolymer surfaces.

[0005] Fluoropolymers are readily used in medical devices in combination with elastomeric components, in part due to their very non-reactive physical properties. However, the use of fluoropolymers is typically minimized to film coatings and more typically to partial film coatings of such elastomeric components, due to the relatively high cost of the fluoropolymer material itself. As such, elastomeric components manufactured with partial fluoropolymer coatings also have exposed surfaces with no fluoropolymer coating. These exposed or uncoated elastomeric surfaces render such components difficult to process, such as by automated assembly equipment/processes, due to the relatively high coefficient of friction of the exposed elastomeric material. This is problematic as, for example, glass or plastic containers are widely used with elastomeric closures for pharmaceutical products and are manufactured with automated high-speed assembly equipment.

[0006] Thus, such components typically require the use of additional compounds, such as silicone oil lubricants, to be coated onto the surfaces of these components to allow for improved efficiencies in the manufacturing of such components and products therefrom. However, the use of lubricants, such as silicone oils, causes additional problems. For example, silicone oils used to coat elastomeric pharmaceutical container closures can result in added particle debris (such as silicone gel globules), can adversely effect or interact with the contents of the pharmaceutical container, or can adversely effect instrumentation that may be used in conjunction with the pharmaceutical container (such as automated blood analyzers).

[0007] Accordingly, there is still a need for a method to satisfactorily coat materials having a fluoropolymer surface or a fluoropolymer surface in combination with a high coefficient of friction surface with a material without the need and adverse effects of lubricants, such as silicone oil. The present invention satisfies this need.

BRIEF SUMMARY OF THE INVENTION

[0008] In accordance with the present invention, the problem of adding lubricity to components with fluoropolymer surfaces and without lubricants, such as silicone oil, is solved by coating such components with polyxylylene.

[0009] One aspect of the present invention relates to a method of coating polyxylylene on a fluoropolymer surface comprising etching the fluoropolymer surface and depositing polyxylylene on the etched fluoropolymer surface.

[0010] According to another aspect, the present invention relates to a method of coating a substrate with polyxylylene comprising providing a substrate; providing a fluoropolymer laminate; etching the fluoropolymer laminate; laminating the etched fluoropolymer laminate on at least a portion of the substrate; and depositing polyxylylene on the etched fluoropolymer laminate and the substrate.

[0011] According to a further aspect, the present invention relates to an elastomeric device comprising: an elastomeric substrate; an etched fluoropolymer film laminated on at least a portion of the elastomeric substrate; and a polyxylylene coated on the elastomeric substrate and the fluoropolymer film.

[0012] According to yet another aspect, the present invention relates to a syringe comprising: a lubricant-free syringe barrel; a piston rod; and a lubricant-free syringe piston slidingly engaged with the syringe barrel and connected to the piston rod, the lubricant-free syringe piston including: a fluoropolymer film laminated on at least a portion of the piston; and a polyxylylene coating formed by etching the fluoropolymer surface and depositing polyxylylene on the etched fluoropolymer surface on at least a portion of the fluoropolymer film.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0013] The foregoing summary, as well as the following detailed description of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0014] Fig. 1 is a schematic, cross-sectional, elevational view of an etched fluoropolymer layer in accordance with one embodiment of the present invention;

[0015] Fig. 2 is a schematic, cross-sectional, elevational view of the fluoropolymer layer of Fig. 1 etched on both sides;

[0016] Fig. 3 is a schematic, cross-sectional, elevational view of the etched fluoropolymer layer of Fig. 1 with a polyxylylene layer formed on the etched surface;

[0017] Fig. 4 is a schematic, partially sectional, lateral view of a syringe piston coated with a polyxylylene layer in accordance with another embodiment of the present invention;

[0018] Fig. 5 is a schematic, partially sectional, lateral view of an elastomeric container closure coated with a polyxylylene layer in accordance with yet another embodiment of the present invention; and

[0019] Fig. 6 is a schematic, partially sectional, longitudinal view of a syringe in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] According to a first aspect, the present invention relates to a method of coating a polyxylylene layer on a fluoropolymer surface (*e.g.*, a fluoropolymer substrate, such as a film or any type of device or part of a device. Fluoropolymers are readily known in the art and a detailed description of them is not necessary for a complete understanding of the present embodiment. However, exemplary fluoropolymers can include, but are not limited to, homopolymers and copolymers of tetrafluoroethylene (TFE), perfluoroalkoxy polymer resin (PFA), copolymers of hexafluoropropylene and tetrafluoroethylene, polyethylenetetrafluoroethylene (PETFE), polyvinyl fluoride (PVF), fluorinated ethylene-propylene copolymers (FEP), polyethylenechlorotrifluoroethylene (PECTFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), and derivatives thereof.

[0021] Polyxylylenes applicable to the present invention can be any polyxylylene polymer, derivatives, or isomers thereof. The term polyxylylene is intended to include both polymers and co-polymers of the various polyxylylenes known in the art or to be developed. Exemplary polyxylylene polymers applicable to the present invention include, but are not limited to, those disclosed in U.S. Patent Nos. 3,288,728 and 3,342,754 to Gorham, the disclosures of which are hereby incorporated herein by reference in their entirety. For example, applicable polymers can include copolymers of substituted para-xylylenes, copolymers of substituted p-xylylenes, poly-p-xylylenes, homopolymers of p-xylylenes, and derivatives thereof. Preferably, the polyxylylene is Parylene and derivatives and isomers thereof, manufactured and commercially available from *e.g.*, Specialty Coating Systems, Indianapolis, IN.

[0022] Parylene is a trade name for a series of polyxylylenes manufactured by Specialty Coating Systems. Parylene coatings are formed from vapor-phase deposition and polymerization of para-xylylene (or its substituted derivatives). There are a number of derivatives and isomers of Parylene, such as Parylene N, Parylene C, and Parylene D. Parylene N is a poly-para-xylylene formed from di-p-xylene, a dimer of p-xylene. Parylene C is produced from the same monomer as for Parylene N, but modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. Parylene D is produced from the same monomer as for Parylene N but modified by the substitution of the chlorine atom for two of the aromatic hydrogens.

[0023] Polyxylylenes are highly resistant to chemical attack, have a low coefficient of friction, and can maintain these properties even at ultrathin film thicknesses, such as a few thousand angstroms. Plus, due to their unique properties, polyxylylenes conform to virtually any shape, including sharp edges, crevices, points, or flat and exposed internal surfaces. The coatings remain flexible and are therefore useful for substrates that are subject to flexing or elastomeric substrates.

[0024] In order to sufficiently bond polyxylylenes onto a fluoropolymer surface, the fluoropolymer surface is initially etched to enhance its surface bonding properties. Methods of etching fluoropolymer surfaces can include chemical etching processes (also known as chemical milling or wet etching), plasma etching processes, or any other etching process readily known in the art or to be developed capable of etching fluoropolymer films. An exemplary method of plasma etching fluoropolymer films is disclosed in U.S. Patent No. 4,933,060 to Prohaska *et al.*, the disclosure of which is hereby incorporated herein by reference in its entirety.

[0025] As shown in Figs. 1-3, at least one surface, such as the top surface 16, of a fluoropolymer layer 10 is etched to create an etched surface 12. The etched surface 12 can be formed on a single side of the fluoropolymer layer 10 (as shown in Fig. 1) or on both the top surface 16 and a bottom surface 18 of the fluoropolymer layer 10 (as shown in Fig. 2), or any other surface for a more three dimensional substrate The etched surface 12 is preferably created by chemical or plasma etching processes.

[0026] After the fluoropolymer layer 10 has been etched, polyxylylene 14 is coated onto the etched surface 12, as shown in Fig. 3. The polyxylylene 14 can be deposited or otherwise coated onto the etched surface 12 by vapor deposition (chemical or physical vapor deposition). U.S. Patent No. 3,379,803 to Tittman *et al.*, the disclosure of which is hereby incorporated herein by reference in its entirety, also discloses various methods for applying polyxylylenes to a substrate surface that are applicable to the present invention.

[0027] Preferably, polyxylylene 14 is deposited onto the etched surface 12 by chemical vapor deposition. For example, to deposit Parylene using a vacuum application system, a Parylene dimer is placed in the vacuum system and converted to a reactive vapor of the Parylene monomer. As the Parylene monomer comes into contact with the etched surface 12, typically at room temperature, the Parylene monomer vapor rapidly coats the etched surface

12 in the form of a Parylene polymer having a substantially uniform finish *e.g.*, in coating coverage and thickness. Exemplary chemical vapor deposition (CVD) processes can also include, but are not limited to, atmospheric pressure CVD, low pressure CVD and ultrahigh vacuum CVD.

[0028] Typical processes for the vapor deposition of polyxylylene are well known in the art and a detailed description of their operation, function and structure is not necessary for a complete understanding of the present embodiment. However, exemplary vapor deposition units include a vaporization chamber, a pyrolysis chamber and a deposition chamber. For example, in the vapor deposition of Parylene, Parylene dimer (di-para-xylylene) is vaporized at 150° C and 1 Torr to a dimeric gas in a vaporization chamber. Then in a pyrolysis chamber, the gas is pyrolized to cleave the dimer to its monomeric form (para-xylylene) at 680° C and 0.5 Torr. Thereafter, in a deposition chamber, the monomer is deposited to form the polymer film (poly[para-xylylene]) at 25° C and 0.1 Torr.

[0029] The polyxylylene coating 14 can be manufactured to a variety of coating thicknesses, including thicknesses below 0.2 microns, while still maintaining their physical and chemical properties. Preferably, the coating thickness is from about 0.05 to about 2 microns and more preferably from about 0.2 to about 2 microns.

[0030] The following specific, non-limiting examples illustrate the present invention for the method of coating polyxylylene onto fluoropolymer surfaces.

EXAMPLE 1

[0031] FluroTec® film, a PTFE (fluoropolymer) film initially etched on one side, was plasma etched on the non-etched side by either a hydrogen based or vinyl benzene based plasma method. The etched PTFE film was then molded onto 10 cc plungers (manufactured from 4405/58 Gray stock *i.e.*, an elastomer) with the plasma etched side facing the mold. The PTFE film was placed in the mold for 2 minutes to heat up and then molded to the 10 cc plungers at 325° F for seven (7) minutes. Parts were then trimmed and washed. The plungers molded with the etched PTFE film were then coated with Parylene N at a target thickness of 0.25 μm. On the Parylene coated parts, the Parylene layer completely adhered to both the PTFE film and the exposed portions of the plunger material itself.

EXAMPLE 2

[0032] FluroTec® stoppers (*i.e.*, stoppers having a fluoropolymer coating manufactured by West Pharmaceutical Services, Inc., of Lionville, PA) were etched and coated with Parylene by deposition using a dimer of Parylene N. The FluroTec® stoppers were etched with a chemical etchant FluoroEtch® (*i.e.*, sodium naphthalene complex in glycol ether) by Acton Technologies of Pittston, PA, for about 2 minutes. The stoppers were then coated with Parylene by deposition using a dimer of Parylene N with a resultant average coating thickness of about 0.32 μm. Unetched stoppers (control samples) were coated with Parylene using the same procedure as for etched FluroTec® stoppers. The etched FluroTec® stoppers exhibited complete adhesion of the Parylene coating onto the stoppers. The Parylene coating on etched FluroTec® stoppers could not be removed by scraping while the Parylene coating on unetched FluroTec® stoppers was easily peeled off when scraped.

EXAMPLE 3

[0033] Syringe plunger tips having a PETFE (fluoropolymer) coating were etched with FluoroEtch® for about 2 minutes. The etched plunger tips were then coated with a layer of Parylene by deposition using a dimer of Parylene N at different thicknesses resulting in an average coating thickness of about 0.27 μm, 0.43 μm, or 0.55 μm. Unetched plunger tips (control samples) were also coated with Parylene N having an average resulting thickness of about 0.26 μm. The Parylene coating on etched plunger tips exhibited complete adhesion. The Parylene coating on etched plunger tips could not be separated from the PETFE coating but could be separated from unetched plunger tips.

[0034] According to a second aspect, the present invention relates to a method of coating substrates, such as an elastomeric base, a device, *etc.*, with polyxylylene. For exemplary purposes only, the method will now be described as applied to coating a substrate in the form of a piston 20, as shown in Fig. 4. The method includes providing a substrate *i.e.*, piston 20, and a fluoropolymer laminate 32. The fluoropolymer laminate 32 is etched, such as by a plasma etching or chemical etching process. The fluoropolymer laminate 32 can be etched on either a top side (or top surface) or both the top side and a bottom side of the fluoropolymer laminate 32. The etched fluoropolymer laminate 32 is laminated onto the piston 20, so as to completely or partially cover the outside surfaces of the piston 20. That is, the etched fluoropolymer laminate 32 can be laminated on only a portion of the piston 20 substrate.

Polyxylylene, such as Parylene, is then deposited, as described in the first aspect of the present invention above, onto the etched fluoropolymer laminate 32 and the piston 20.

[0035] According to a third aspect, the present invention relates to an elastomeric device that includes an elastomeric substrate or base, an etched fluoropolymer film laminated to or molded to at least a portion of the elastomeric substrate surface, and a polyxylylene coating that is coated onto the elastomeric base and the fluoropolymer film. The elastomeric device can be, for example, a medical device, a closure, a syringe piston, a seal, a gasket, a plunger tip, a component of a pre-filled syringe, a sleeve stopper, a flashback bulb, a cap, a liner, a washer, or any other device from which such an elastomeric substrate can be constructed, such as baby bottle nipples, or elastomeric members which can be in contact with pharmaceutically pure materials. The polyxylylene can be formed to completely coat the elastomeric device. In manufacturing the elastomeric device, the polyxylylene can be applied to the fluoropolymer film before or after the fluoropolymer film is laminated or molded onto the elastomeric substrate. The method of laminating or molding the fluoropolymer film onto the elastomeric substrate is well known in the art, and a detailed explanation of such methods is not necessary for a complete understanding of the present embodiment. However, an exemplary method of molding fluoropolymer films onto elastomeric components is by compression molding. The method of coating the polyxylylene onto the elastomeric substrate and the fluoropolymer surface is as described in the first aspect of the present invention above.

[0036] Fig. 4 illustrates a syringe piston 20 embodiment in accordance with the present invention. The syringe piston 20 includes a distal end 22, a proximal end 24, an elastomeric piston base 26, internal female threads 28 for engaging a syringe rod (not shown), and ribs 30. The elastomeric piston base 26 can be of any configuration readily known in the art for a syringe piston 20. The elastomeric piston base 26 is partially laminated with a fluoropolymer film 32 on its distal end 22. Alternatively, the piston base 26 or a portion thereof can be formed of a fluoropolymer, rather than from an elastomer having an etched fluoropolymer film laminated thereon. A polyxylylene coating 34 *e.g.*, Parylene, is then coated on the entire exterior surface of the elastomeric piston base 26 after etching of the fluoropolymer film 32. Alternatively, the polyxylylene coating 34 can be coated on only a portion of the piston base 26 and a portion of the etched fluoropolymer film 32. As a result, the present embodiment can provide a syringe piston 20 partially laminated with a fluoropolymer film 32 having an added polyxylylene coating 34 to improve the components overall lubricity without the need for additional lubricants, such as silicone oil.

[0037] The syringe piston 20 of the present exemplary embodiment advantageously provides polyxylylene 34 coated onto an elastomeric piston base 26 partially laminated with a fluoropolymer film 32. That is, the polyxylylene 34 coating is on both the piston base 26 partially laminated with a fluoropolymer film 32 and the non-laminated portions of the piston base 26. Moreover, polyxylylene 34 is coated onto the fluoropolymer film 32 without the need for any intervening adhesive layer, since the pre-etching provides the necessary adherence. This advantageously allows the syringe piston 20 to take advantage of the polyxylylene coating's surface characteristics of high surface energy and lubricity (*i.e.,* a low coefficient of friction). As such, the syringe piston 20 in accordance with the present embodiment does not require any additional lubricant, such as silicone oil, along the uncoated surfaces *e.g.*, side ribs 36 of the piston 20 to effectively slide along the interior wall of a syringe barrel (Fig. 6). The application of the polyxylylene coating 34 on such elastomeric devices, such as syringe piston 20, further advantageously provides lubricity to the components as they are processed in a production assembly line to manufacture a finished component. That is, the added lubricity provided by the polyxylylene coating 34 to such elastomeric components facilitates the movement of parts in assembly equipment (such as filling and stoppering operations) and reduces the number of rejects and machine down-time associated with components that do not have such lubricity characteristics or are not lubricated. Moreover, the present embodiment eliminates the need for any lubricating operation for elastomeric components necessary for processing such components.

[0038] Fig. 5 illustrates a stopper or closure 40 embodiment in accordance with the present invention. The closure 40 includes an elastomeric closure base 42, a top surface 44, a bottom end 46, an etched fluoropolymer film 48 laminated onto *e.g.*, the bottom end 46 of the elastomeric closure base 42, and a polyxylylene coating 50 *e.g.*, Parylene, covering the entire surface area of the elastomeric closure 40 including the areas laminated with the fluoropolymer film 48 which has previously been etched. Alternatively, the polyxylylene coating 50 can be coated on a portion (*i.e.*, less than the entire exterior surface) of the elastomeric closure base 42 and fluoropolymer film 48. The elastomeric closure base 42 can be configured as any closure readily known in the art. In a preferred embodiment, the closure

40 is configured to be a test tube closure or a closure for evacuated tubes, such as evacuated blood collection tubes.

[0039] In manufacturing the closure 40, the fluoropolymer film 48 laminated onto the bottom end 46 can be etched before or after being laminated onto the elastomeric closure base 42. The polyxylylene coating 50 is then formed on *e.g.*, the entire outside surface of the closure 40, including the fluoropolymer film surfaces, by *e.g.*, chemical vapor deposition.

[0040] Similar to the syringe piston example above, the closure 40 would advantageously eliminate the need for any lubricant, such as silicone oil, for the processing, assembly, or operation of the closure device. This is especially advantageous for applications in medical devices. For instance, it is commonly known that silicone lubricants used on evacuated blood collection tubes can have adverse effects on test results and analytical instruments used for blood assays.

[0041] According to a fourth aspect, the present invention relates to a "lubricant-free" syringe 100, as shown in Fig. 6. That is, the syringe 100 does not include any lubricant, such as silicone oil (*i.e.*, "silicone-free"), for lubricating either the syringe piston 106, syringe barrel 102 or syringe piston rod 104. In this embodiment, the syringe 100 can be a glass syringe, a plastic syringe with a needle hub assembly, a staked needle syringe, or a syringe for use in an auto-injector. The syringe piston 106 can be coated as previously described above for syringe piston 20 and as shown in Fig. 4. In particular, the syringe barrel 102 is a lubricant-free syringe barrel 102 and the syringe piston 106 is a lubricant-free syringe piston 106. The lubricant-free syringe piston is connected to the piston rod 104 and configured to slidingly engage with the lubricant-free syringe barrel 102. The lubricant-free syringe piston 106 further includes an etched fluoropolymer film laminated on at least a portion of the piston 106, and a polyxylylene coating on at least a portion of the fluoropolymer film and a surface of the piston 106 not laminated by the fluoropolymer film.

[0042] In summary, the various aspects of the present invention advantageously allow for the elimination of lubricants, such as silicone oil, from components having a partial fluoropolymer surface, provide improved coating adhesion of polyxylylene to fluoropolymer surfaces, and enable improved manufacturability and mechanical function of elastomeric and other devices where reduced friction is required or desired without the need for lubricants, such as silicone oil. Moreover, the present invention would eliminate the need all together for the addition of lubricants, such as silicone oil, on pharmaceutical seals and elastomeric components (*e.g.,* stoppers, syringe pistons, *etc.*) partially having a fluoropolymer surface.

[0043] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

I claim:

1. A method of coating polyxylylene on a fluoropolymer surface comprising:
etching the fluoropolymer surface; and
depositing polyxylylene on the etched fluoropolymer surface.

2. The method of claim 1, wherein the fluoropolymer surface is at least one of polytetrafluoroethylene, perfluoroalkoxy polymer, fluorinated ethylene-propylene polymer, ethylene tetrafluoroethylene polymer, fluorinated ethylene propylene polymer, polyvinyl fluoride polymer, copolymers of hexafluoropropylene and tetrafluoroethylene, polyethylenechlorotrifluoroethylene, polyvinylidene fluoride, polychlorotrifluoroethylene, and derivatives thereof.

3. The method of claim 1, wherein the polyxylylene is selected from a Parylene and derivatives and isomers thereof.

4. The method of claim 1, wherein the etching comprises at least one of plasma etching and chemical etching.

5. The method of claim 1, wherein the etching comprises etching a top surface and a bottom surface of a fluoropolymer layer.

6. The method of claim 1, wherein the depositing step comprises chemical vapor deposition or physical vapor deposition of the polyxylylene on the fluoropolymer surface.

7. A method of coating substrates with polyxylylene comprising:
providing a substrate;
providing a fluoropolymer laminate;
etching the fluoropolymer laminate;
laminating the etched fluoropolymer laminate on at least a portion of the substrate; and
depositing polyxylylene on the etched fluoropolymer laminate and the substrate.

8. The method of claim 7, wherein the etched fluoropolymer laminate is laminated only on a portion of the substrate

9. An elastomeric device comprising:

an elastomeric substrate;

an etched fluoropolymer film laminated on at least a portion of the elastomeric substrate; and

a polyxylylene coated on the elastomeric substrate and the fluoropolymer film.

10. The elastomeric device of claim 9, wherein the elastomeric base is selected from a medical device, a closure, a syringe piston, a seal, a gasket, a plunger tip, a sleeve stopper, a flashback bulb, a cap, a liner and a washer.

11. A syringe comprising:

a lubricant-free syringe barrel;

a piston rod; and

a lubricant-free syringe piston slidingly engaged with the syringe barrel and connected to the piston rod, the lubricant-free syringe piston including:

a fluoropolymer film laminated on at least a portion of the piston; and

a polyxylylene coating formed in accordance with claim 1, on at least a portion of the fluoropolymer film.

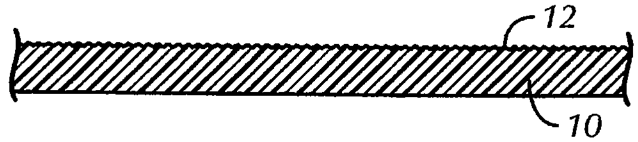

FIG. 1

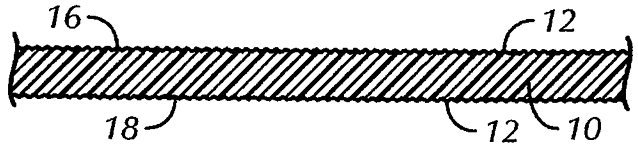

FIG. 2

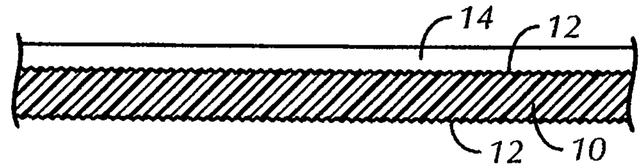

FIG. 3

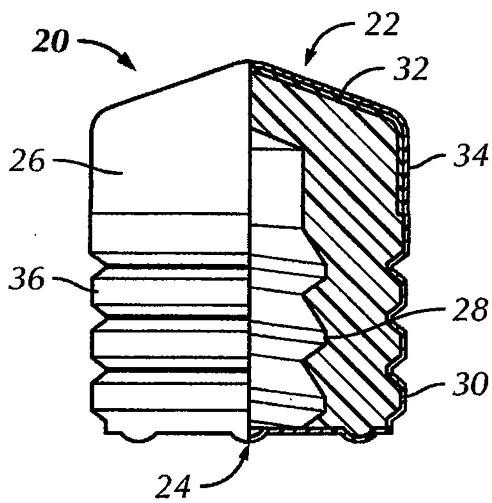

FIG. 4

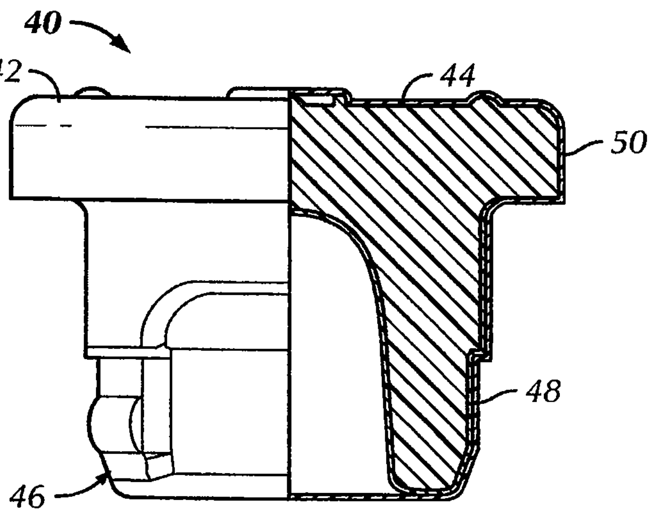

FIG. 5

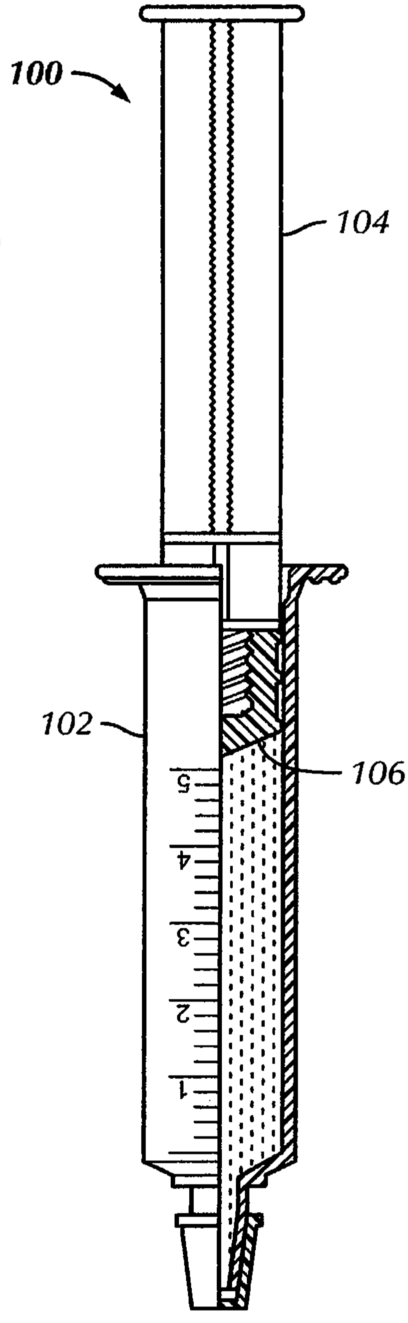

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/048851

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/18

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)
C08J

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.
Y	US 3 379 803 A (TITTMANN FREDERICK R; JAYNE JR WILLIAM M) 23 April 1968 (1968-04-23) cited in the application claim 1; examples	1-11
Y	US 4 933 060 A (PROHASKA GEORGE W [US]; BUTLER RICHARD J [US]; NICKOSON CARL G [US]) 12 June 1990 (1990-06-12) cited in the application claims; examples	1-11
A	US 5 288 504 A (VERSIC RONALD J [US]) 22 February 1994 (1994-02-22) claim 1	1

☐ 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

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 September 2009	16/09/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	West, Nuki

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/048851

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3379803 A	23-04-1968	DE 1646153 A1	18-03-1971
		GB 1112894 A	08-05-1968
		NL 6505685 A	05-11-1965
US 4933060 A	12-06-1990	NONE	
US 5288504 A	22-02-1994	US 5393533 A	28-02-1995