construction. The "actual volume" at any given time will vary according to whether the machine 10 has just been used to prepare a beverage, what type of beverage it was used for and whether a steam purge cycle has been run. Thus the improved brew cycle control incorporates means for varying the volume of gas in the delivery system according to the type of beverage to be dispensed (i.e. one requiring a crema with smaller and fewer bubbles or one which requires a greater froth of larger bubbles) taking into account the actual volume of gas already present. The means for varying the volume of gas may be achieved by combinations of:-

1. purging the delivery system after a brewing cycle is complete, and prior to a subsequent high pressure brew, which will increase the gas:liquid ratio;
2. venting gas from the delivery system prior to high pressure brewing, which will decrease the gas:liquid ratio; and
3. inducting gas into the delivery system prior to high pressure brewing, which will increase the gas:liquid ratio.

Valve means are preferably provided to enable the volume of gas within the delivery system to be reduced and an air pump to enable gas (typically air) to be injected into the system. A separate, dedicated air valve may be incorporated in the delivery system, either upstream or downstream of the cartridge 100. Preferably the variable geometry valve 60 described above may be used as the valve means.

To enable this improved brew cycle control to be effected, additional parameters to those described in connection with the basic machine 10 may be stored in the memory of the control processor. These additional parameters include the basic volume of gas for the specific construction of machine 10 (which will apply to the machine 10 which is unused or after it has been purged) and the volume required during high pressure brewing for optimising the crema for each specific beverage. Preferably the additional parameters also include the actual volume of gas which will remain in the delivery system after each type of brew operation which the machine 10 is capable of. However this is not wholly necessary if the machine 10 is programmed to run a steam purge cycle after every beverage is dispensed, which effectively resets the actual volume to the basic volume, because it flushes the dispensing system downstream of the water heater 13 of any remaining liquid.

The brew cycle will therefore include an additional step, namely a gas adjustment cycle before the pre-wet cycle. The gas adjustment cycle thus includes:-

1. An assessment of the required volume of gas for the type of beverage to be prepared. This will most conveniently be the selection from the processor memory of the required parameter associated with the cartridge code 120;

2. The determination of the actual volume of gas currently resident in the delivery means according to the

last operation of the machine 10. This will be the basic volume for an unused machine or if a purge cycle has been run. If the machine has just been used to prepare a beverage and no purge cycle run, the processor ideally selects from the memory the parameter for the remaining gas according to the last beverage. Alternatively, means may also be provided to specifically monitor the volume of gas within the delivery system at any point in time;

3. A calculation of the volume of gas to be inducted into or vented from the delivery system to achieve the required volume;

4. The modification of the volume of gas, if required, by the induction of additional gas (typically air) or the venting of excess gas.

In one example the beverage preparation machine 10 has a basic volume of gas of 36ml in the section of the delivery means extending between the water heater 13 and the beverage ingredients 200.

There are a number of different modes of operation for step 4 depending on the outcome of step 3, depending on what type of valve means are used. If the valve means are downstream of the cartridge, i.e. an outlet valve, one way of controlling the volume of air upstream of the beverage ingredients 200 prior to high pressure brewing is by closing the outlet valve at different points in the brew cycle as follows:-

1. The Correct Volume of Gas is Present

If the processor calculates that it requires the full basic volume of gas (36ml) for the beverage to be dispensed, as determined from the reading of the code 120, it closes the outlet valve at the start of the brew cycle, before any water flows from the water heater 13. This means that the compression of gas in the delivery system will commence immediately and the cartridge 100 will be subject to higher pressures during the pre-wet and soak cycles, with the valve only opening to dispense the resultant beverage. As the outlet valve is closed before the pump 14 is started, all of the 36ml of trapped gas is mixed in to the resulting beverage and a larger volume of slightly coarser crema is obtained (Figure 16a). In the example shown the volume of crema Y in a graduated glass, flat bottomed beaker was 20ml compared to the volume of liquid X, which was 50ml.

The chart shown in Figure 16b represents an example of brew cycle parameters used to produce a beverage in this mode with a large volume of crema under test conditions.

In this chart, a stop condition of 0 seconds (e.g. against the remove gas step) indicates that the step is not carried out.

2. Too Much Gas is Present

If, on the other hand, a beverage with a small volume of crema is indicated by the cartridge 100 inserted and there is an excess of gas present in the system, the outlet

valve is closed after the pump 14 has operated for a short time until the excess gas in the delivery system has escaped through the open valve at low pressure. With the valve being closed later in the brew cycle, the required volume of gas is vented to atmosphere via the cartridge 100 and valve, so a smaller quantity of trapped gas is left to be compressed and mixed in to the resulting beverage during high pressure brewing and consequently a smaller volume of finer crema is obtained (Figure 17a). In the example shown the volume of crema Y in a graduated glass, flat bottomed beaker was 5ml compared to the volume of liquid X, which was 50ml.

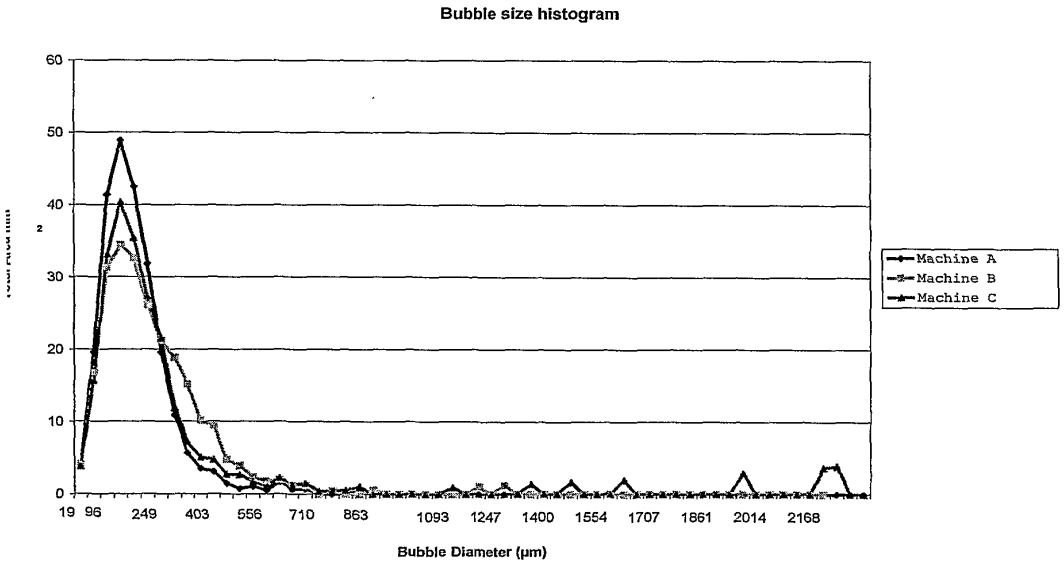
The chart shown in Figure 17b represents an example of brew parameters used to produce a beverage in this mode with a small volume of crema under test conditions.

3. Insufficient Gas Present

If step 3 indicates that more gas needs to be inducted, the outlet valve is closed immediately and the air pump operated until the deficit has been made up. Thereafter high pressure brewing commences.

The following graph is a digital image analysis showing a comparison of the crema characteristics produced by the present beverage preparation machine 10 (machine A) utilising the gas management system and two prior art machines (machines B and C) without such gas management system. Comparing the profiles for each machine from the peak (~172µm diameter) rightwards (increasing bubble size), it can be seen that machine A exhibits a very tight

distribution of small bubbles within the crema. Machine C (the Nespresso Latissma (tm)which is a high pressure machine which has a pressure rating of around 19 bar and operates at a pressure between 9 and 15 bar) produces a broader/coarser distribution with a number of larger diameter bubbles, whilst machine B (the applicant's own Tassimo/Bosch Machine(tm) similar to that described in EP-A-1440644 which is a low pressure machine operating at pressures below 2 bar) is coarser still, though without the larger bubbles seen for machine C.



The tail to the left of the chart (extremely small bubbles) is characteristic of the limits of the image analysis systems used to produce the graph, though is qualitatively similar.

Some elements of the control of the gas in the beverage machine 10 may also be effected manually by the use of suitable buttons for the user to press, to indicate the type of beverage being produced and the required crema characteristics.

Whilst this improvement has been described with reference to beverage machines 10 which use cartridges 100, it may also be used in bulk brewers and other non-cartridge machines.

Embodiments of cartridges 100 which are suitable for use in the machine 10 having the improvements described above are shown in Figures 18 to 30.

The cartridge 100 generally comprises an outer member 102, an inner member 103 and a laminate 105. The outer member 102, inner member 103 and laminate 105 are assembled to form the cartridge 100 which has an interior 106 for containing one or more beverage ingredients, an inlet 107, an outlet 108 and a beverage flow path linking the inlet 107 to the outlet 108 and which passes through the interior 106. The inlet 107 and outlet 108 are initially sealed by the laminate 105 and are opened in use by piercing or cutting of the laminate 105. The beverage flow path is defined by spatial inter-relationships between the outer member 102, inner member 103 and laminate 105 as discussed below. Other components may optionally be included in the cartridge 100, such as a filter 104, as will be described further below.

A first version of cartridge 100 which will be described is shown in Figures 19 to 29. The first version of the cartridge 100 is particularly designed for use in dispensing espresso-style products such as roast and ground coffee where it is desirable to produce a crema. However, this version of the cartridge 100 may be used with other products such as chocolate, coffee, tea, sweeteners, cordials, flavourings, alcoholic beverages, flavoured milk, fruit juices, squashes, sauces and desserts.

As can be seen from Figure 23, the overall shape of the cartridge 100 is generally circular or disc-shaped with the diameter of the cartridge 100 being significantly greater than its height. A major axis X passes through the centre of the outer member as shown in Figure 19. Typically the overall diameter of the outer member 102 is 74.5 mm ±6mm and the overall height is 16 mm ±3mm. Typically the volume of the cartridge 100 when assembled is 30.2 ml ±20%.

The outer member 102 generally comprises a bowl-shaped shell 110 having a curved annular wall 113, a closed top 111 and an open bottom 112. The diameter of the outer member 102 is smaller at the top 111 compared to the diameter at the bottom 112, resulting from a flaring of the annular wall 113 as one traverses from the closed top 111 to the open bottom 112. The annular wall 113 and closed bottom 112 together define a receptacle having an interior 134.

A hollow inwardly directed cylindrical extension 118 is provided in the closed top 111 centred on the major axis X. As more clearly shown in Figure 20, the cylindrical

extension 18 comprises a stepped profile having first, second and third portions 119, 120 and 121. The first portion 119 is right circular cylindrical. The second portion 120 is frusto-conical in shape and is inwardly tapered. The third portion 121 is another right circular cylinder and is closed off by a lower face 131. The diameter of the first, second and third portion 119, 120 and 121 incrementally decreases such that the diameter of the cylindrical extension 118 decreases as one traverses from the top 111 to the closed lower face 131 of the cylindrical extension 118. A generally horizontal shoulder 132 is formed on the cylindrical extension 118 at the junction between the second and third portions 120 and 121.

An outwardly extending shoulder 133 is formed in the outer member 102 towards the bottom 112. The outwardly extending shoulder 133 forms a secondary wall 115 co-axial with the annular wall 113 so as to define an annular track forming a manifold 116 between the secondary wall 115 and the annular wall 113. The manifold 116 passes around the circumference of the outer member 102. A series of slots 117 are provided in the annular wall 113 level with the manifold 116 to provide gas and liquid communication between the manifold 116 and the interior 134 of the outer member 102. As shown in Figure 21, the slots 117 comprise vertical slits in the annular wall 113. Between twenty and forty slots are provided. In the embodiment shown thirty-seven slots 117 are provided generally equi-spaced around the circumference of the manifold 16. The slots 117 are preferably between 1.4 and 1.8 mm in length. Typically the length of each slot 117 is 1.6 mm representing 10% of the overall height of the

outer member 102. The width of each slot 117 is between 0.25 and 0.35 mm. Typically, the width of each slot 117 is 0.3 mm. The width of the slots 117 is sufficiently narrow to prevent the beverage ingredients passing there through into the manifold 116 either during storage or in use.

An inlet chamber 126 is formed in the outer member 102 at the periphery of the outer member 102. A cylindrical wall 127 is provided, as most clearly shown in Figure 23, which defines the inlet chamber 126 within, and partitions the inlet chamber 126 from, the interior 134 of the outer member 102. The cylindrical wall 127 has a closed upper face 128 which is formed on a plane perpendicular to the major axis X and an open lower end 129 co-planar with the bottom 12 of the outer member 102. The inlet chamber 26 communicates with the manifold 116 via two slots 130 as shown in Figure 19. Alternatively, between one and four slots may be used to communicate between the manifold 116 and the inlet chamber 126.

A lower end of the outwardly extending shoulder 133 is provided with an outwardly extending flange 135 which extends perpendicularly to the major axis X. Typically the flange 135 has a width of between 2 and 4 mm. A portion of the flange 135 is enlarged to form a handle 124 by which the outer member 102 may be held. The handle 124 is provided with an upturned rim 125 to improve grip.

The outer member 102 is formed as a single integral piece from high density polyethylene, polypropylene, polystyrene, polyester, or a laminate of two or more of

these materials. A suitable polypropylene is the range of polymers available from DSM UK Limited (Redditch, United Kingdom). The outer member may be opaque, transparent or translucent. The manufacturing process may be injection moulding.

The inner member 103 as shown in Figures 25 to 28, comprises an annular frame 141 and a downwardly extending cylindrical funnel 140. A major axis X passes through the centre of the inner member 103 as shown in Figure 25.

As best shown in Figures 26 and 27, the annular frame 141 comprises an outer rim 151 and an inner hub 152 joined by ten equi-spaced radial spokes 153. The inner hub 152 is integral with and extends from the cylindrical funnel 140. Filtration apertures 155 are formed in the annular frame 141 between the radial spokes 153. A filter 104 is disposed on the annular frame 141 so as to cover the filtration apertures 155. The filter is preferably made from a material with a high wet strength, for example a non-woven fibre material of polyester. Other materials which may be used include a water-impermeable cellulosic material, such as a cellulosic material comprising woven paper fibres. The woven paper fibres may be admixed with fibres of polypropylene, polyvinyl chloride and/or polyethylene. The incorporation of these plastic materials into the cellulosic material renders the cellulosic material heat-sealable. The filter 104 may also be treated or coated with a material which is activated by heat and/or pressure so that it can be sealed to the annular frame 141 in this way.

As shown in the cross-sectional profile of Figure 25, the inner hub 152 is located at a lower position than the outer rim 151, resulting in the annular frame 141 having a sloping lower profile.

The upper surface of each spoke 153 is provided with an upstanding web 154 which divides a void space above the annular frame 141 into a plurality of passages 157. Each passage 157 is bounded on either side by a web 154 and on a lower face by the filter 104. The passages 157 extend from the outer rim 151 downwardly towards, and open into, the cylindrical funnel 140 at openings 156 defined by the inner extremities of the webs 154.

The cylindrical funnel 140 comprises an outer tube 142 surrounding an inner discharge spout 143. The outer tube 142 forms the exterior of the cylindrical funnel 140. The discharge spout 143 is joined to the outer tube 142 at an upper end of the discharge spout 143 by means of an annular flange 147. The discharge spout 143 comprises an inlet 145 at an upper end which communicates with the openings 156 of the passages 157 and an outlet 144 at a lower end through which the prepared beverage is discharged into a cup or other receptacle. The profile of the discharge spout 43 comprises a stepped profile with a distinct dog-leg 166 near an upper end of the tube 143.

As shown in Figure 25, the discharge spout 143 is provided with a partition 165 which extends part way up the discharge spout 143 from the outlet 144. The partition 165

helps to prevent the beverage spraying and/or splashing as it exits the discharge spout 143.

A rim 167 is provided upstanding from the annular flange 147 joining the outer tube 142 to the discharge spout 143. The rim 167 surrounds the inlet 145 to the discharge spout 143 and defines an annular channel 169 between the rim 167 and the upper portion of the outer tube 142. The rim 167 is provided with an inwardly directed shoulder 168. At one point around the circumference of the rim 167 an aperture 170 is provided in the form of a slot which extends from an upper edge of rim 167 to a point marginally below the level of the shoulder 168 as most clearly shown in Figures 25 and 25a. The slot has a width of 0.64 mm.

An air inlet 171 is provided in annular flange 147 circumferentially aligned with the aperture 170 as shown in Figures 28 and 28a. The air inlet 171 comprises an aperture passing through the flange 147 so as to provide communication between a point above the flange 147 and the void space below the flange 147 between the outer tube 142 and discharge spout 143. Preferably, and as shown, the air inlet 171 comprises an upper frusto-conical portion 173 and a lower cylindrical portion 172. The air inlet 171 is typically formed by a mould tool such as a pin. The tapered profile of the air inlet 171 allows the mould tool to be more easily removed from the moulded component. The wall of the outer tube 142 in the vicinity of the air inlet 171 is shaped to form a chute leading from the air inlet 171 to the inlet 145 of the discharge spout 143. As shown in Figure 28a, a canted shoulder 174 is formed between the air inlet

171 and the chute to ensure that the jet of beverage issuing from the slot 170 does not immediately foul on the upper surface of the flange 147 in the immediate vicinity of the air inlet 171.

The inner member 103 may be formed as a single integral piece from polypropylene or a similar material as described above and by injection moulding in the same manner as the outer member 102.

Alternatively, the inner member 103 and/or the outer member 102 may be made from a biodegradable polymer. Examples of suitable materials include degradable polyethylene (for example, SPITEK supplied by Symphony Environmental, Borehamwood, United Kingdom), biodegradable polyester amide (for example, BAK 1095 supplied by Symphony Environmental), poly lactic acids (PLA supplied by Cargil, Minnesota, USA), starch-based polymers, cellulose derivatives and polypeptides.

The laminate 105 is formed from two layers, a first layer of aluminium and a second layer of cast polypropylene. The aluminium layer is between 0.02 and 0.07 mm in thickness. The cast polypropylene layer is between 0.025 and 0.065 mm in thickness. In one embodiment the aluminium layer is 0.06 mm and the polypropylene layer is 0.025 mm thick. This laminate 105 is particularly advantageous as it has a high resistance to curling during assembly. As a result the laminate 105 may be pre-cut to the correct size and shape and subsequently transferred to the assembly station on the production line without undergoing distortion. Consequently,

the laminate 108 is particularly well suited to welding. Other laminate materials may be used including PET/Aluminium/PP, PE/EVOH/PP, PET/metallised/PP and Aluminium/PP laminates. Roll laminate stock may be used instead of die cut stock.

The cartridge 100 may be closed by a rigid or semi-rigid lid instead of a flexible laminate 105.

Assembly of the cartridge 100 involves the following steps:

a) the inner member 103 is inserted into the outer member 102;
b) the filter 104 is cut to shape and placed onto the inner member 103 so to be received over the cylindrical funnel 140 and come to rest against the annular frame 141;
c) the inner member 103, outer member 102 and filter 104 are joined by ultrasonic welding;
d) the cartridge 100 is filled with one or more beverage ingredients;
e) the laminate 105 is affixed to the outer member 102.

These steps will be discussed in greater detail below.

The outer member 103 is orientated with the open bottom 112 directed upwards. The inner member 103 is then inserted into the outer member 102 with the outer rim 151 being received as a loose fit in an axial extension 114 at top 111 of the cartridge 100. The cylindrical extension 118 of the

outer member 102 is at the same time received in the upper portion of the cylindrical funnel 140 of the inner member 103.

The third portion 121 of the cylindrical extension 118 is seated inside the support rim 167. The shoulder 132 of the cylindrical extension 118 between the second portion 120 and third portion 121 bears against the upper edge of the support rim 167 of the inner member 103. An interface zone is thus formed between the inner member 103 and the outer member 102 comprising a face seal between the cylindrical extension 118 and the support rim 167 which extends around nearly the whole circumference of the cartridge 100. The seal between the cylindrical extension 118 and the support rim 167 is not fluid-tight though since the slot 170 in the support rim 167 extends through the support rim 167 and downwardly to a point marginally below the shoulder 168. Consequently the interface fit between the cylindrical extension 118 and the support rim 167 transforms the slot 170 into an aperture providing gas and liquid communication between the annular channel 169 and the discharge spout 143. The aperture is typically 0.64 mm wide by 0.69 mm long.

The filter 104 is then placed over the inner member 103 such that the filter material contacts the annular rim 151. An ultrasonic welding process is then used to join the filter 104 to the inner member 103 and at the same time, and in the same process step, the inner member 103 to the outer member 102. The inner member 103 and filter 104 are welded around the outer rim 151. The inner member 103 and outer

member 102 are joined by means of weld lines around the outer rim 151 and also the upper edges of the webs 154.

As shown most clearly in Figure 29, the outer member 102 and inner member 103 when joined together define a void space in the interior 106 below the annular flange 141 and exterior the cylindrical funnel 140 which forms a filtration chamber. The filtration chamber 160 and passages 157 above the annular frame 141 are separated by the filter paper 104.

The filtration chamber 160 contains the one or more beverage ingredients 200. The one or more beverage ingredients 200 are packed into the filtration chamber 160. For an espresso-style beverage the ingredient is typically roast and ground coffee. The density of packing of the beverage ingredients in the filtration chamber 130 can be varied as desired. Typically, for a filtered coffee product the filtration chamber contains between 5.0 and 10.2 grams of roast and ground coffee in a filtration bed of thickness of typically 5 to 14 mm. Optionally, the interior 106 may contain one or more bodies, such as spheres, which are freely movable within the interior 106 to aid mixing by inducing turbulence and breaking down deposits of beverage ingredients during discharge of the beverage.

The laminate 105 is then affixed to the outer member 102 by forming a weld 161 around the periphery of the laminate 105 to join the laminate 105 to the lower surface of the outwardly extending flange 135. The weld 161 is extended to seal the laminate 105 against the lower edge of the cylindrical wall 127 of the inlet chamber 126. Further,

a weld 162 is formed between the laminate 105 and the lower edge of the outer tube 142 of the cylindrical funnel 140. The laminate 105 forms the lower wall of the filtration chamber 160 and also seals the inlet chamber 126 and cylindrical funnel 140. However, a small gap 163 exists prior to dispensation between the laminate 105 and the lower edge of the discharge spout 43. A variety of welding methods may be used, such as heat and ultrasonic welding, depending on the material characteristics of the laminate 105.

Advantageously, the inner member 103 spans between the outer member 102 and the laminate 105. The inner member 103 is formed from a material of relative rigidity, such as polypropylene. As such, the inner member 103 forms a load-bearing member that acts to keep the laminate 105 and outer member 102 spaced apart when the cartridge 100 is compressed. It is preferred that the cartridge 100 is subjected to a compressive load of between 130 and 280N in use. The compressive force acts to prevent the cartridge failing under internal pressurisation and also serves to squeeze the inner member 103 and outer member 102 together. This ensures that the internal dimensions of passageways and apertures in the cartridge 100 are fixed and unable to change during pressurisation of the cartridge 100.

In use the water, under pressure, enters the cartridge 100 through the inlet 107 into the inlet chamber 126. From there the water is directed to flow through the slots 117 and round the manifold 116 and into the filtration chamber 160 of the cartridge 1 through the plurality of slots 117. The water is forced radially inwardly through the filtration

chamber 160 and mixes with the beverage ingredients 200 contained therein. The water is at the same time forced upwardly through the beverage ingredients 200. The beverage formed by passage of the water through the beverage ingredients 200 passes through the filter 104 and filtration apertures 155 into the passages 157 lying above the annular frame 141.

Beverage in the radial passages 157 flows downwardly along the passages 157 formed between the webs 154 and through the openings 156 and into the annular channel 169 of the cylindrical funnel 140. From the annular channel 169 the beverage is forced under pressure through the aperture 128 by the back pressure of beverage collecting in the filtration chamber 160 and passages 157. The beverage is thus forced through aperture as a jet and into an expansion chamber formed by the upper end of the discharge spout 143. As shown in Figure 29, the jet of beverage passes directly over the air inlet 171. Passage of the beverage through the restriction of the aperture causes the pressure of the beverage to be reduced. As the beverage enters the discharge spout 143 the pressure of the beverage is still relatively low. As a result air is entrained into the beverage stream in the form of a multitude of small air bubbles as the air is drawn up through the air inlet 171. The jet of beverage issuing from the aperture is funnelled downwards to the outlet 144 where the beverage is discharged into a receptacle such as a cup where the air bubbles form the desired crema. Thus, the aperture and the air inlet 171 together form an eductor which acts to entrain air into the beverage. Flow of beverage into the eductor should be kept

as smooth as possible to reduce pressure losses. It should be noted that, in the high pressure state, the air eduction mechanism is de-activated.

The sealing of the filter 104 onto the spokes 153 and the welding of the rim 151 with the outer member 102 ensures that there are no short-circuits and all the beverage has to pass through the filter 104.

Figure 30 shows a second embodiment of beverage cartridge 100 which can be used in the beverage preparation machine 10 of the present invention. Like components between the first and second embodiments have been referenced with like numerals. Many of the components and functions of the second embodiment of cartridge 100 are the same as for the first embodiment. However, it can be seen from Figure 30 that the cartridge 100 has a greater overall height compared to the cartridge 100 shown in Figure 29. The outer member 102 is taller and thereby defines a larger void space in which a larger quantity of beverage ingredients 200 can be stored. The second embodiment of cartridge 100 is therefore suitable for dispensing larger volumes of beverage. The diameter of the outer member 102 and cartridge 100 are the same as in the first embodiment. Typically the storage volume of the cartridge 100 when assembled is 50 to 58 ml ±20%. As with the first embodiment, the upper surface of the outer member 102 is provided with a recess having a clamping surface 118 located at a bottom thereof. According to the present invention, the separation D between surface 118a and the underside of the laminate 105 is the same as for the first embodiment. As a result, the elongated recess extends

approximately 60% of the distance towards the laminate 105. This advantageously allows for a simplified clamping arrangement to be used as described below.

Also, the second embodiment of cartridge 100 lacks an eductor air inlet 171.

The first and second embodiments of cartridge 1 described above are given as examples of an "eductor" type of cartridge and a "non-eductor" type cartridge which may be used with the improved beverage preparation machine described above.

CLAIMS:

1. A method of preparing beverages using a beverage preparation machine for preparing beverages from one or more beverage ingredients, characterised by controlling the volume of air resident in at least a part of a delivery system of the machine to produce predetermined characteristics in a prepared beverage.

2. A method of preparing beverages as claimed in claim 1 in which the volume of air is actively controlled by increasing the volume to increase the air:liquid ratio in the beverage produced, decreasing the volume to decrease the air:liquid ratio or maintaining the volume.

3. A method of preparing beverages as claimed in any one of the preceding claims in which the volume of air in the delivery system is controlled by inducting additional gas into the delivery system, venting air from the delivery system and/or purging the delivery system.

4. A method of preparing beverages as claimed in any one of the preceding claims further comprising the step of measuring the actual volume of air resident in the delivery system.

5. A method of preparing beverages as claimed in any one of the preceding claims in which an actual volume of air resident in the delivery system is calculated from stored parameters relating to a volume of air remaining in the delivery system after a last operation of the machine.

6. A method of preparing beverages as claimed in any one of the preceding claims in which the control of the volume of air is effected on a beverage by beverage basis.

7. A method of preparing beverages as claimed in any one of the preceding claims in which the control of the volume of air is effected automatically according to the type of beverage being produced.

8. A method of preparing beverages as claimed in any one of claims 1 to 5 in which the control of the volume of a is effected manually.

9. A method of preparing beverages as claimed in any one of the preceding claims in which the volume of air upstream of the beverage ingredients is controlled.

10. A method of preparing beverages as claimed in any one of the preceding claims in which the volume of air downstream of the beverage ingredients is controlled.

11. A method of preparing beverages as claimed in any one of the preceding claims in which the volume of air is controlled by selectively opening and/or closing valve means in the delivery system prior to and/or during beverage preparation.

12. A beverage preparation machine for preparing a beverage from one or more beverage ingredients, characterised by the provision of means for controlling the volume of air

resident in at least a part of a delivery system of the machine to produce predetermined characteristics in a prepared beverage.

13. A beverage preparation machine as claimed in claim 12 further comprising means for determining the actual volume of air resident in the delivery system.

14. A beverage preparation machine as claimed in claim 13 in which the means for determining the actual volume of air resident in the delivery system comprise means for calculating the actual volume from stored parameters relating to a volume of air remaining in the delivery system after a last operation of the machine.

15. A beverage preparation machine as claimed in claim 14 in which the stored parameters comprise a basic volume parameter stored in the control means, said basic volume being the actual volume of air which resides in the delivery system of an unused machine or a machine after a purging cycle has been run.

16. A beverage preparation machine as claimed in claim 14 or claim 15 in which the stored parameters comprise parameters relating to the actual volume of air remaining in the delivery system after each type of beverage which the machine is programmed to prepare.

17. A beverage preparation machine as claimed in claim 13 in which the means for determining the actual volume of air

resident in the delivery system comprise means for measuring the actual volume of air in the delivery system.

18. A beverage preparation machine as claimed in any one of claims 13 to 17 in which parameters relating to predetermined volumes of air required to be present in the delivery system for preparing a predetermined range of beverages are stored in the control means, said control means being programmed to calculate the difference between the predetermined volume required for a beverage in preparation and the actual volume present.

19. A beverage preparation machine as claimed in any one of claims 13 to 18 in which the means for controlling the actual volume of air comprise valve and/or purge means for venting air and/or pump means for injecting additional air into the delivery system.

20. A beverage preparation machine as claimed in claim 19 in which the valve means comprise an outlet valve downstream of the beverage ingredients.

21. A beverage preparation machine as claimed in claim 19 or claim 20 in which the valve means comprise a valve upstream of the beverage ingredients.

22. A beverage preparation machine as claimed in any one of claims 18 to 22 in which the operation of the valve means is controlled relative to the beverage preparation cycle to vary the actual volume of air present in the delivery system.

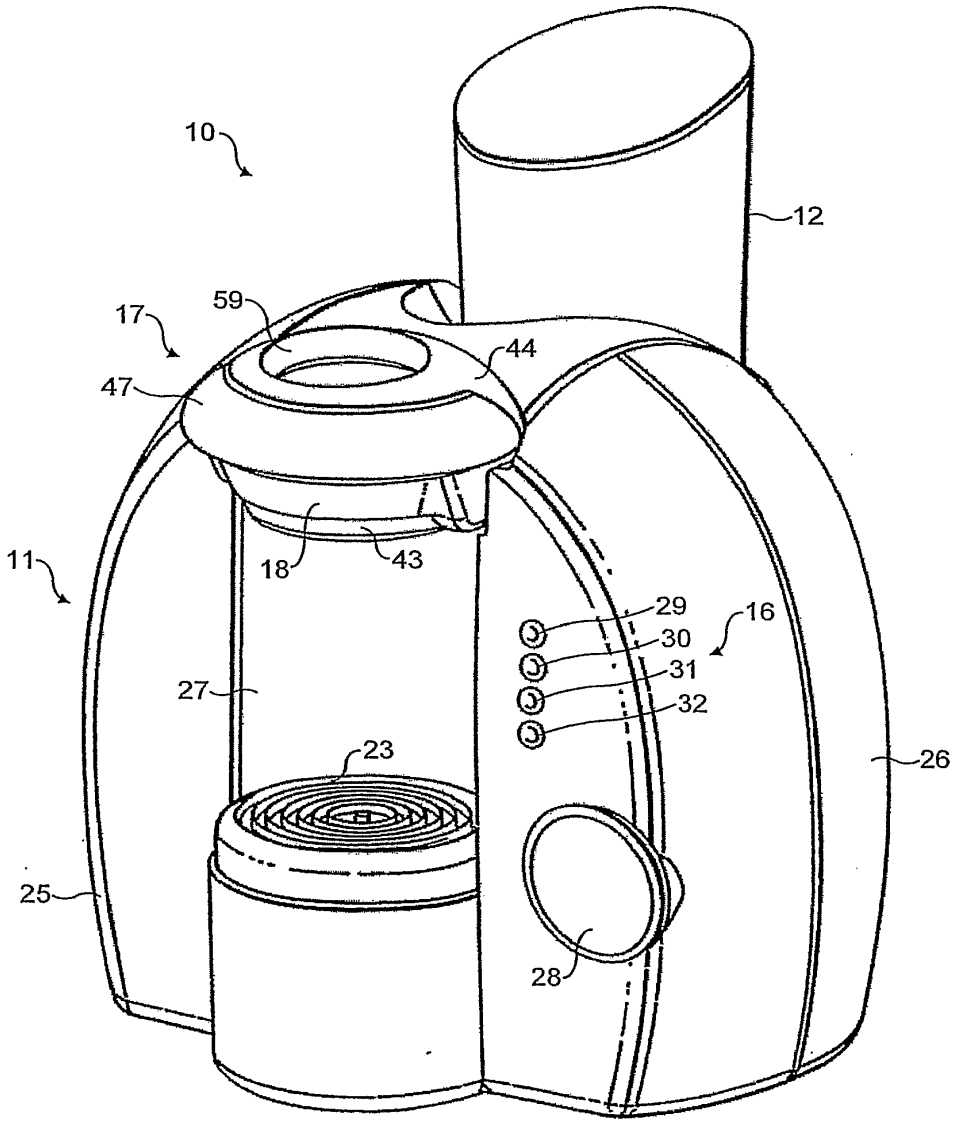


FIG. 1

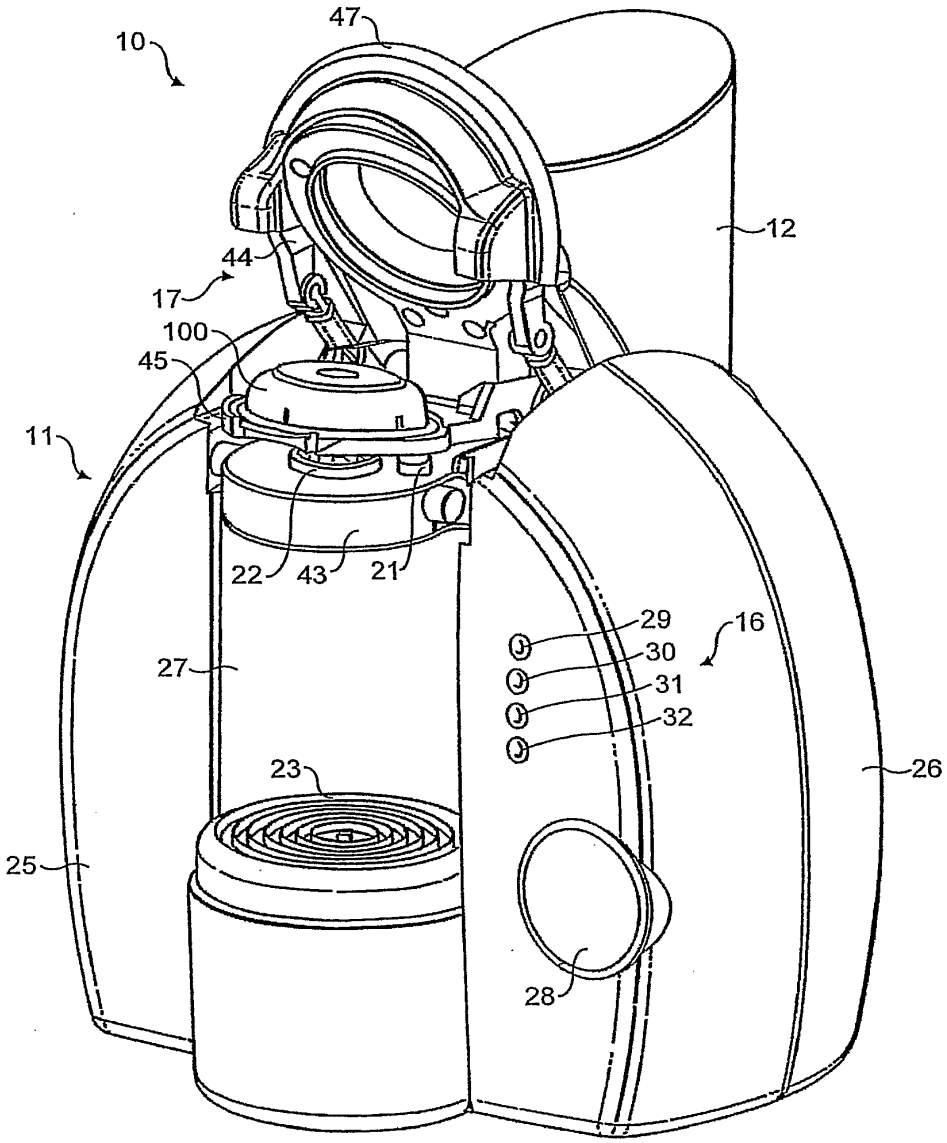


FIG. 2

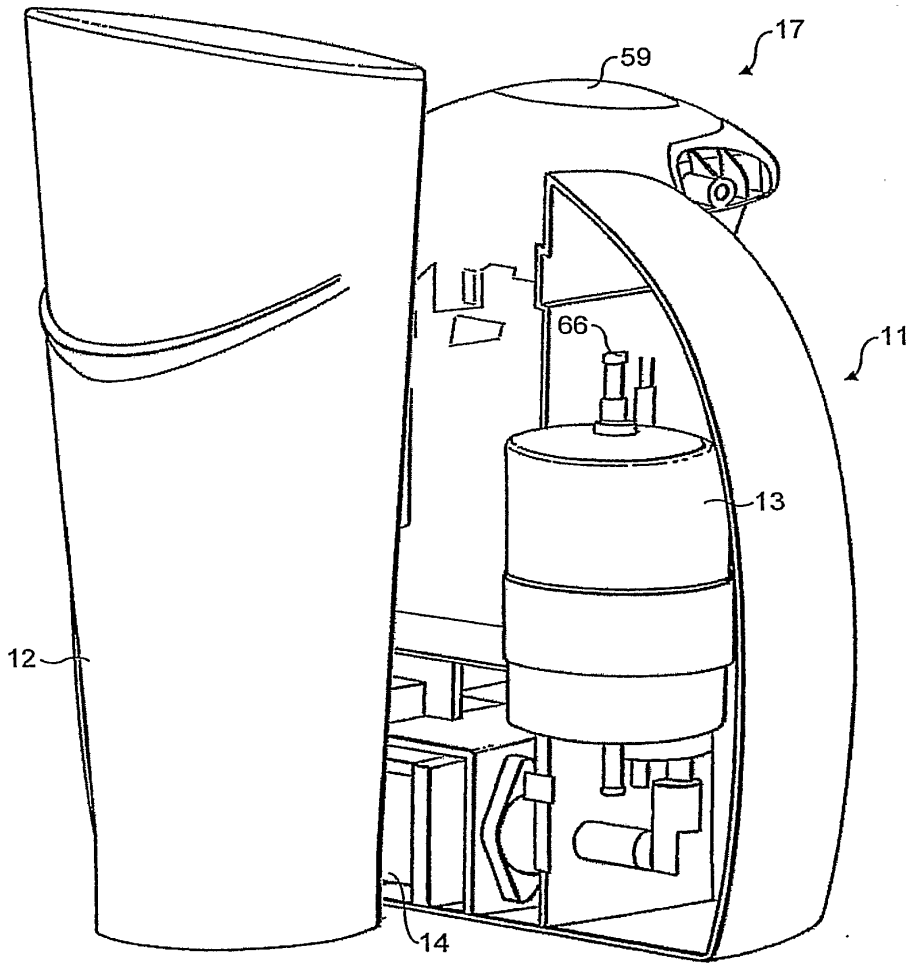


FIG. 3

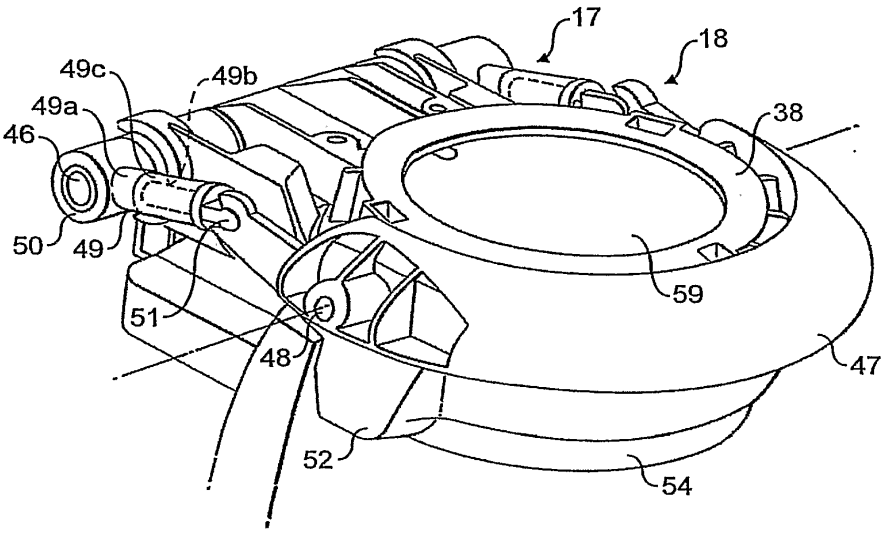

17
18
49c
49b
49a
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38
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59
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FIG. 4

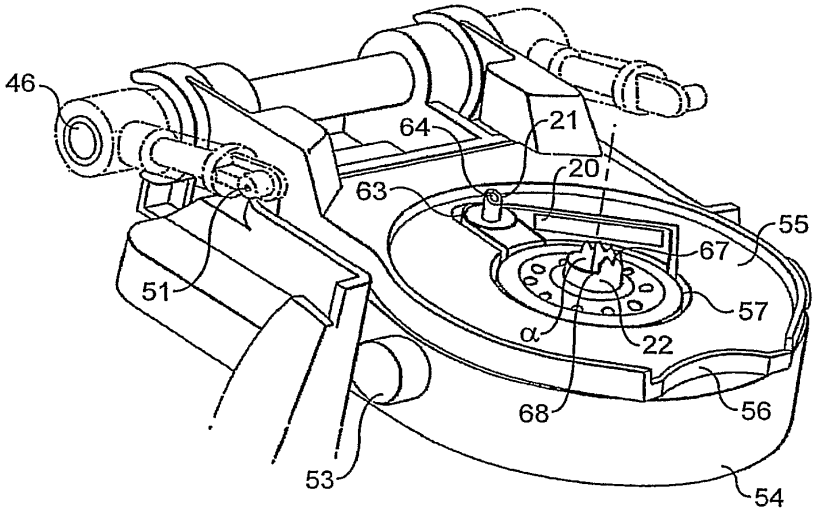

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FIG. 5

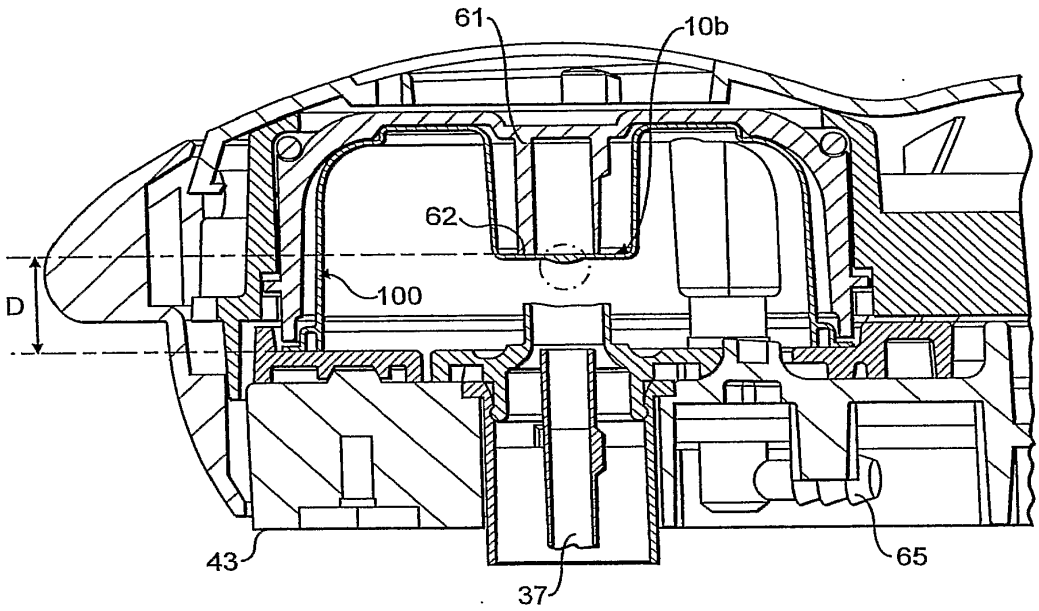


FIG. 6

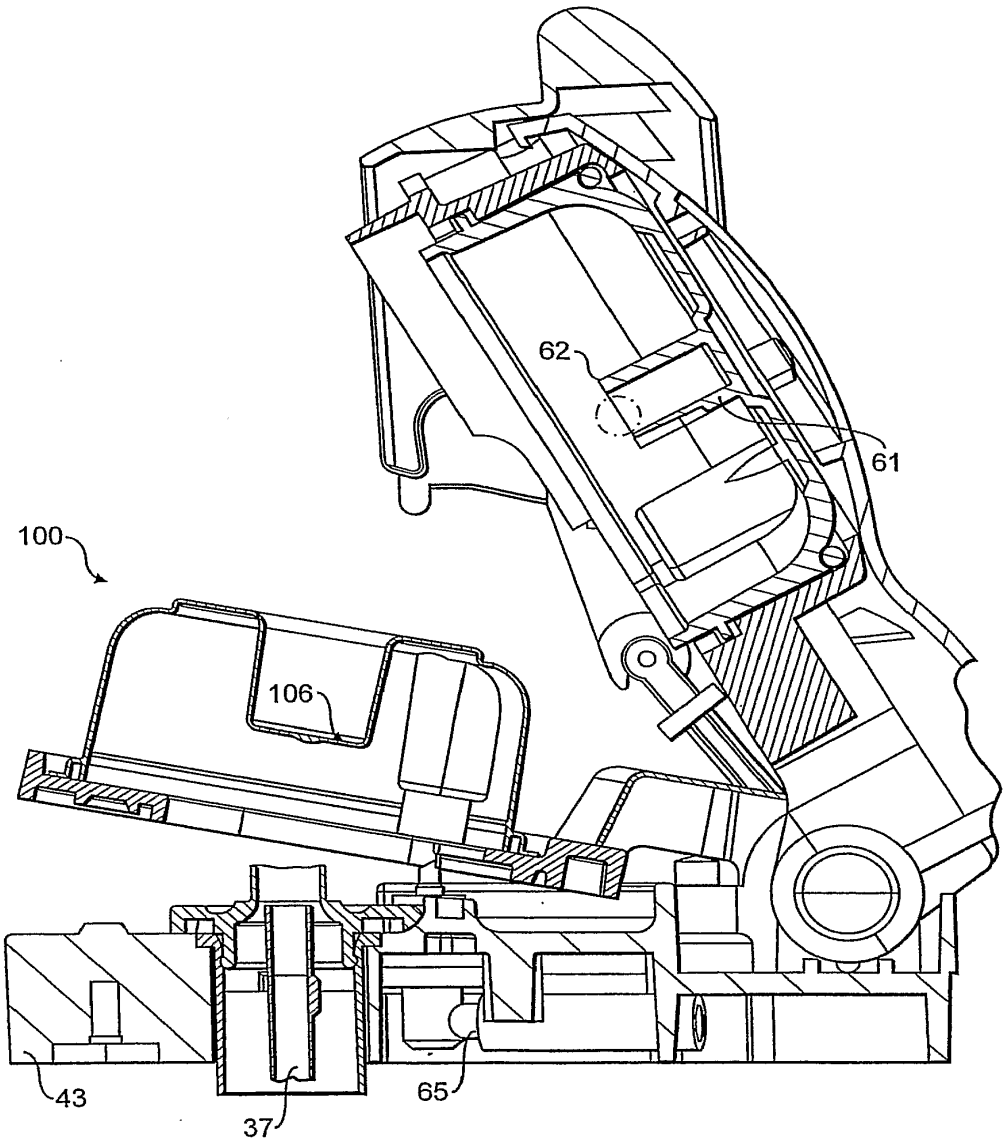


FIG. 7

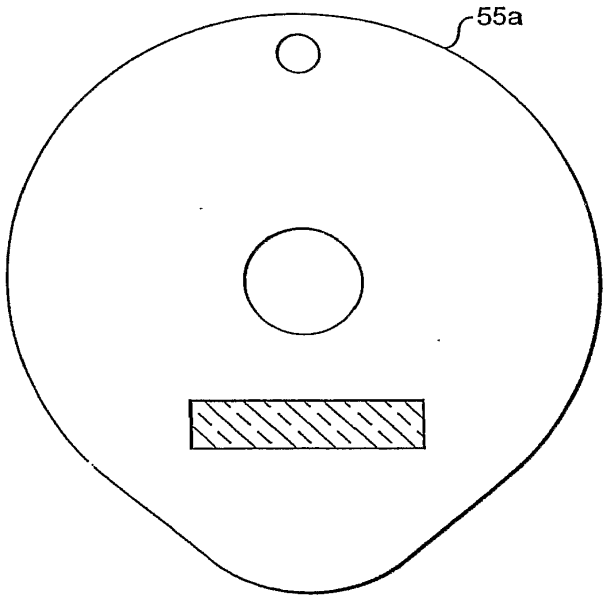


FIG. 7a

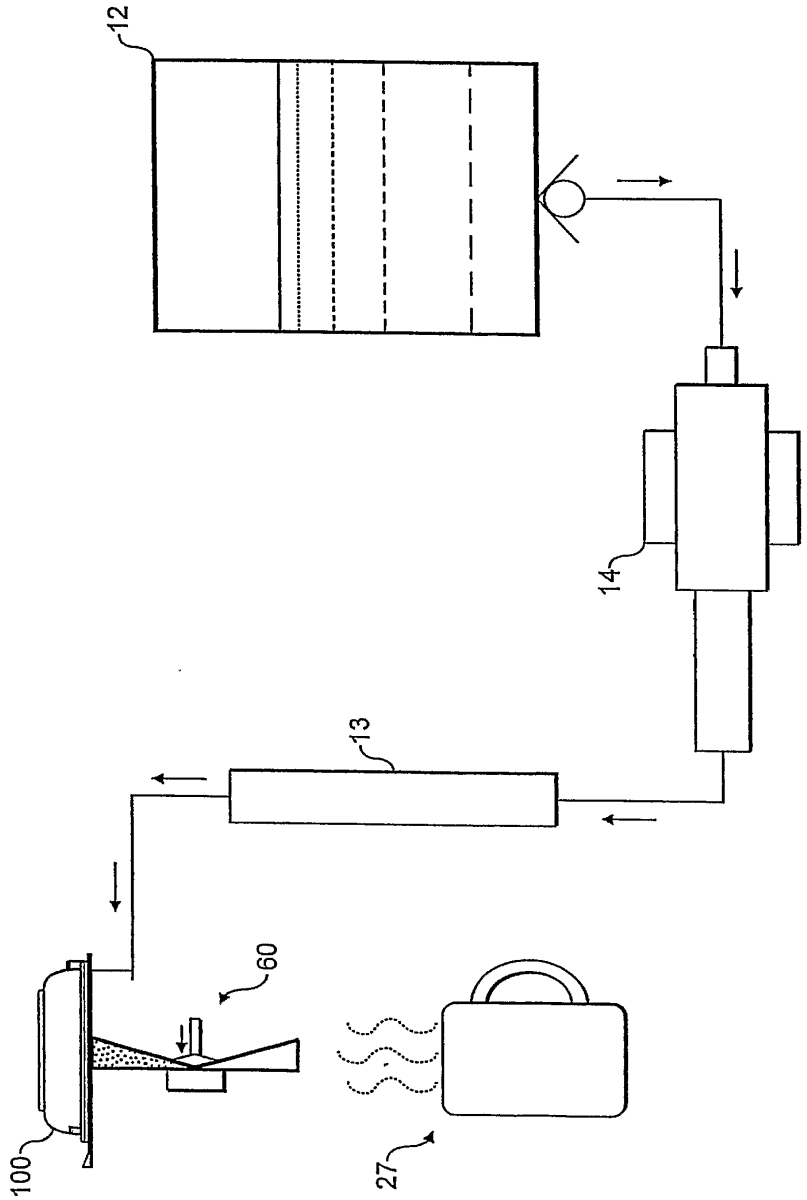


FIG. 8

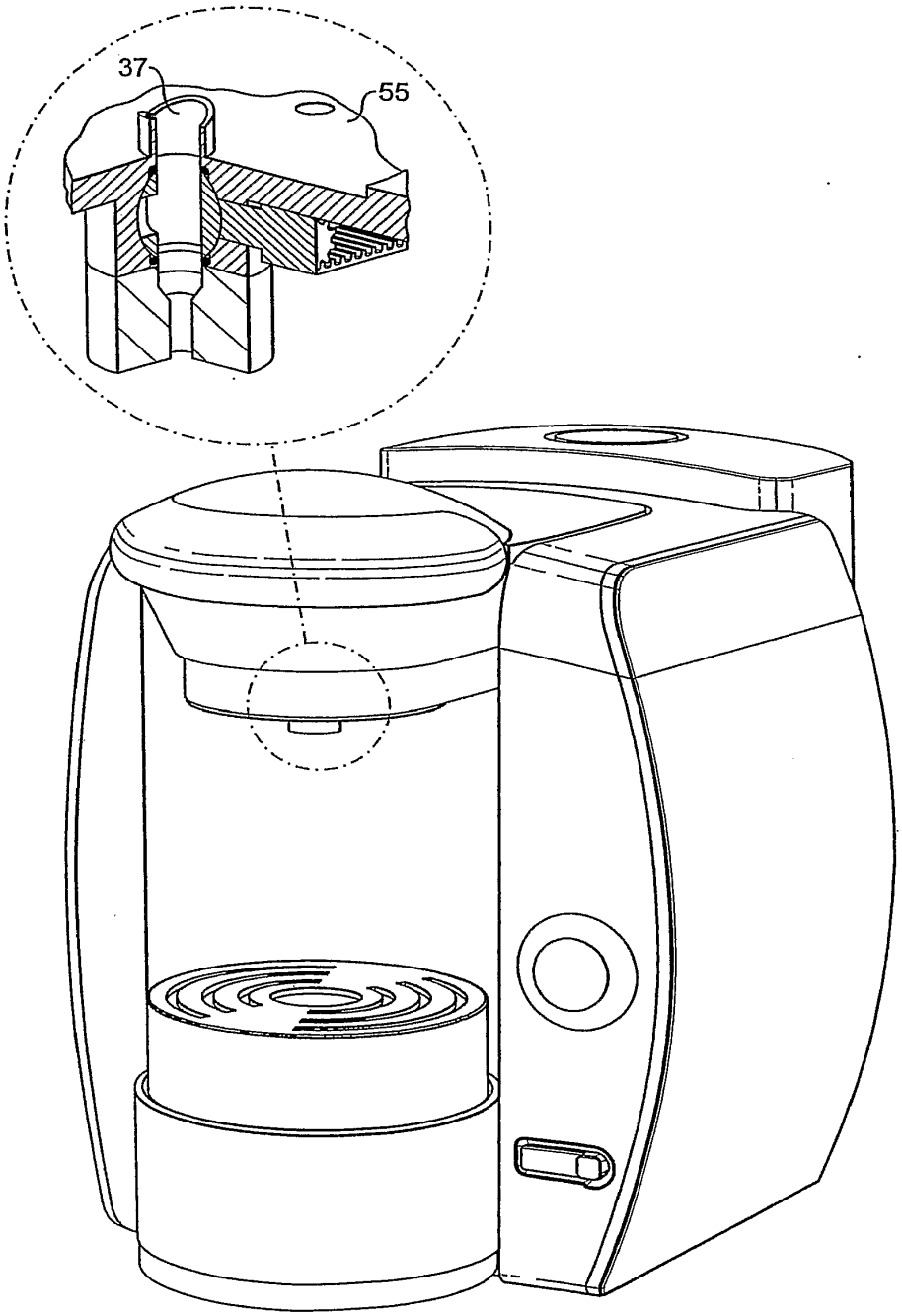


FIG 9

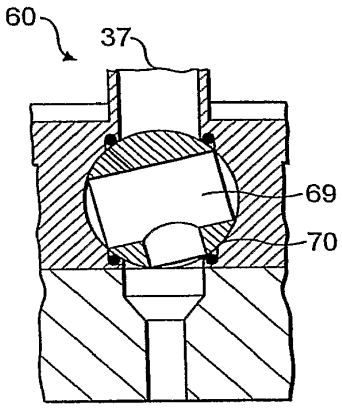


FIG. 10

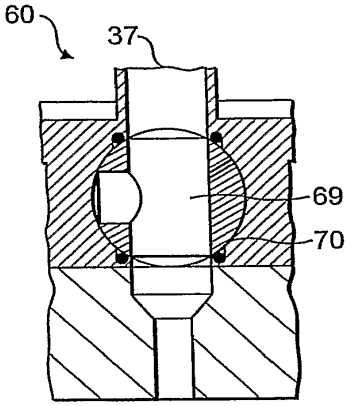


FIG. 11

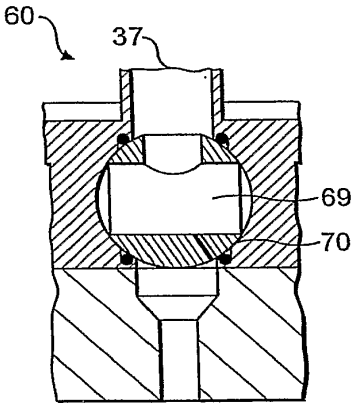


FIG. 12

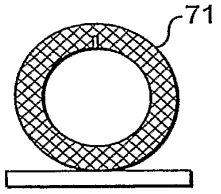


FIG. 13a

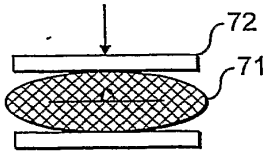


FIG. 13b

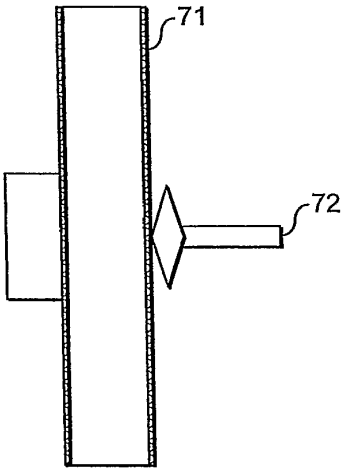


FIG. 14

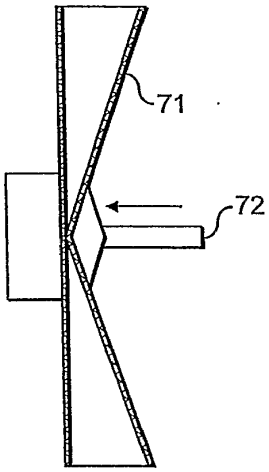


FIG. 15

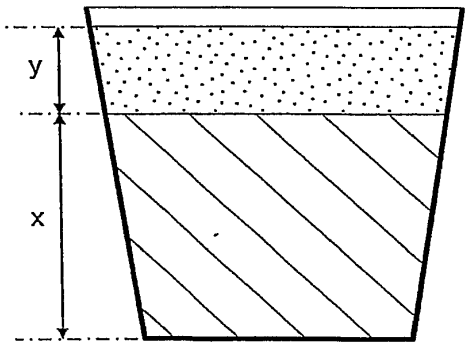


FIG. 16a

STEP	WATER PUMP STATE/SPEED	AIR PURGE PUMP/PWM	RECIRCULATION VALVE STATE	RESTRICTION BYPASS VALVE STATE	STOP CONDITION/DURATION OF STEP
Set valves	No change/0	Stop/0	Recirculate	Open	Time >=1 second
Heat	Stop/0	Stop/0	Recirculate	Open	Boiler temperature >=97°C
Set valves	No change/0	No change/0	Brew	Open	Time >=1 second
Remove gas	Run/50	No change/0	No change	Open	Time >=2 seconds
Set valves	Stop/0	No change/0	No change	Closed	Time >=5 seconds
Pressure wet	Run/100	No change/0	No change	No change	Disc inlet pressure >=2 bar
Soak	Stop/0	No change/0	No change	No change	Time >=10 seconds
Brew	Run/30	Stop/0	No change	No change	Time >=32 seconds
Stop pump	Stop/0	Stop/0	No change	No change	Time >=0.5 seconds
Open purge	Stop/0	Stop/0	No change	Open	Time >=3 seconds
Pause	No change/0	No change/0	No change	Open	Time <=1 seconds
Air purge	Stop/0	Run/50	No change	Open	Time >=8 seconds
Pause	Stop/0	Stop/0	Recirculate	No change	Time >=2 seconds
Reset	Stop/0	Stop/0	Recirculate	Closed	Time >=0 seconds

FIG. 16b

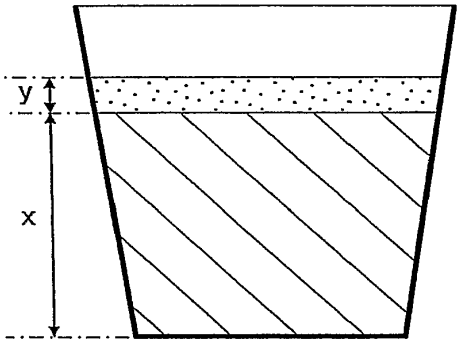


FIG. 17a

STEP	WATER PUMP STATE/SPEED	AIR PURGE PUMP/PWM	RECIRCULATION VALVE STATE	RESTRICTION BYPASS VALVE STATE	STOP CONDITION/DURATION OF STEP
Set valves	No change/0	Stop/0	Recirculate	Open	Time >=1 second
Heat	Stop/0	Stop/0	Recirculate	Open	Boiler temperature >=97°C
Set valves	No change/0	No change/0	Brew	Open	Time >=1 second
Remove gas	Run/70	No change/0	No change	Open	Time >=8 seconds
Set valves	Stop/0	No change/0	No change	Closed	Time >=5 seconds
Pressure wet	Run/100	No change/0	No change	No change	Disc inlet pressure >=2 bar
Soak	Stop/0	No change/0	No change	No change	Time >=10 seconds
Brew	Run/30	Stop/0	No change	No change	Time >=32 seconds
Stop pump	Stop/0	Stop/0	No change	No change	Time >=0.5 seconds
Open purge	Stop/0	Stop/0	No change	Open	Time >=3 seconds
Pause	No change/0	No change/0	No change	Open	Time <=5 seconds
Air purge	Stop/0	Run/50	No change	Open	Time >=8 seconds
Pause	Stop/0	Stop/0	Recirculate	Open	Time >=2 seconds
Reset	Stop/0	Stop/0	Recirculate	Open	Time >=0 seconds

FIG. 17b

K-FEE SYSTEM GMBH, EX2012, page 2150
NESPRESSO USA, INC. v. K-FEE SYSTEM GMBH
IPR2023-00485, U.S. PATENT 11,230,430

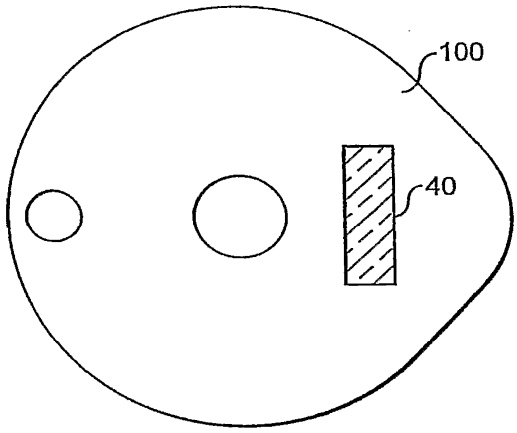

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FIG. 18

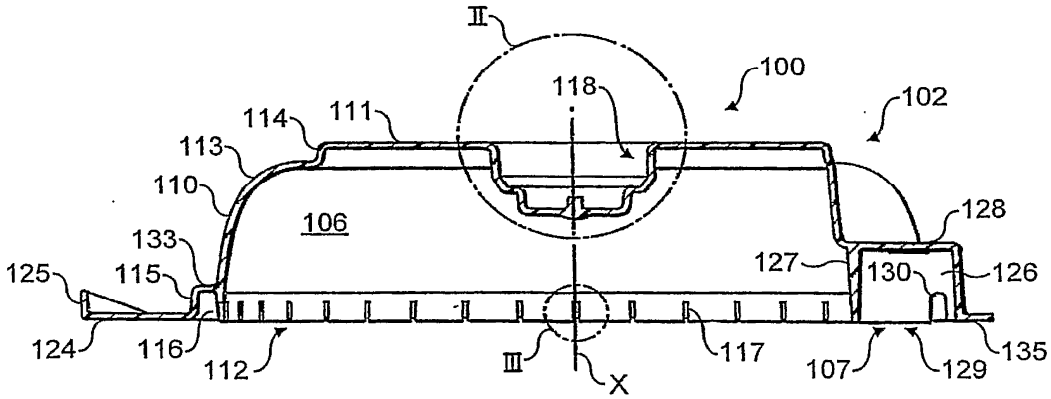

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FIG. 19

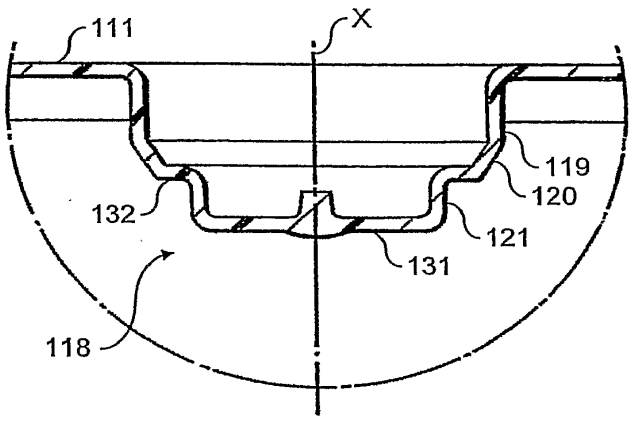


FIG. 20

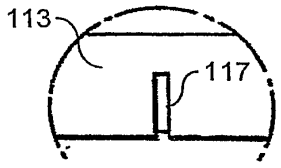


FIG. 21

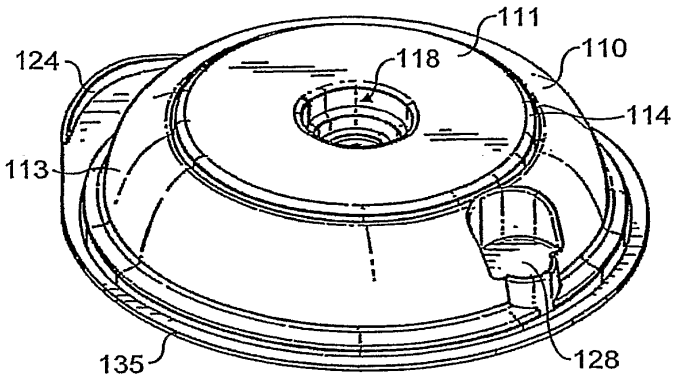


FIG. 22

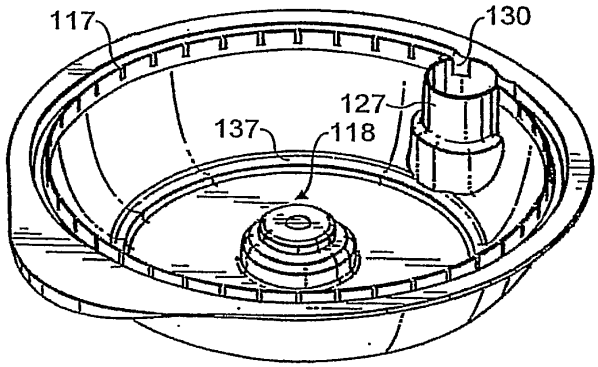


FIG. 23

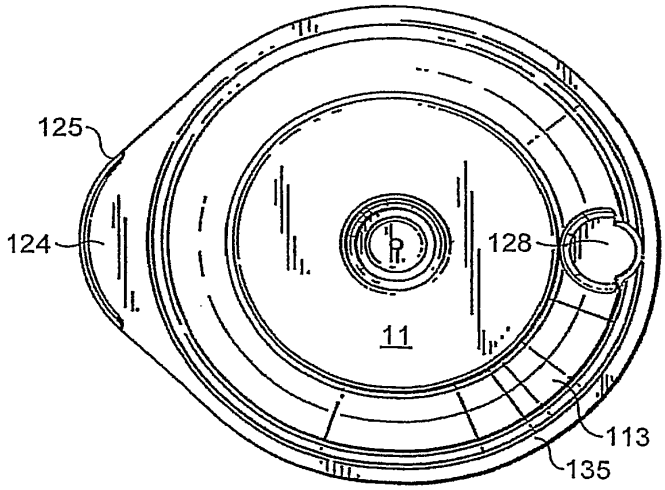


FIG. 24

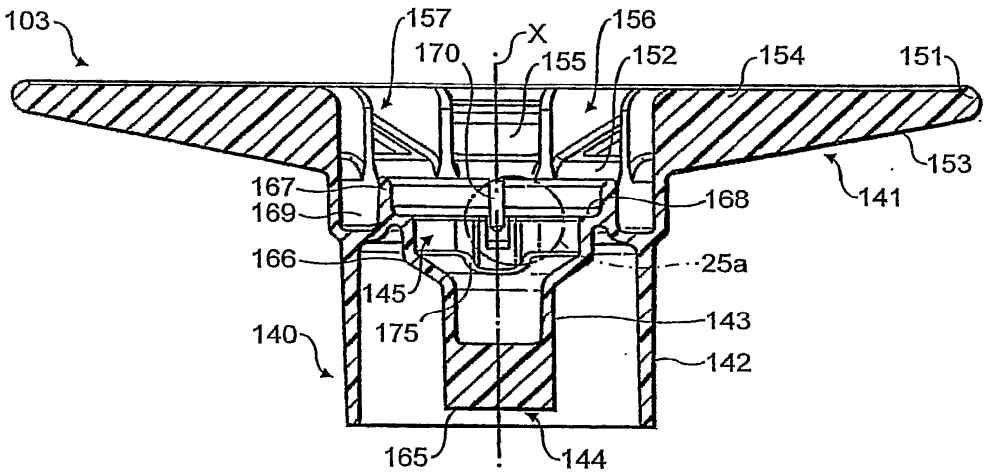


FIG. 25

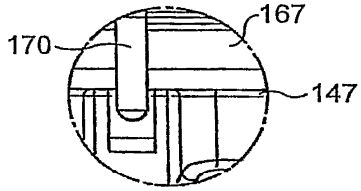


FIG. 25a

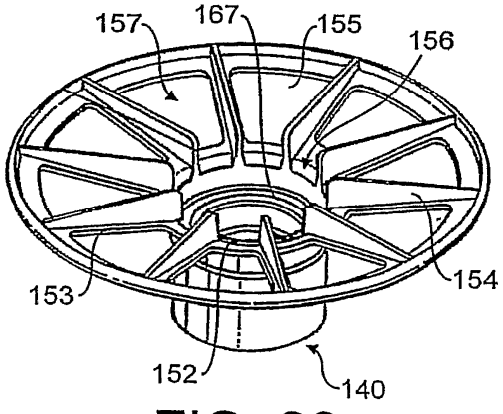


FIG. 26

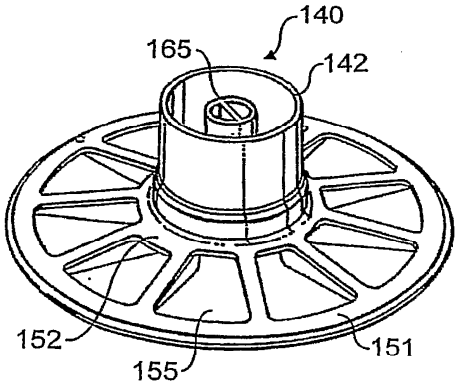


FIG. 27

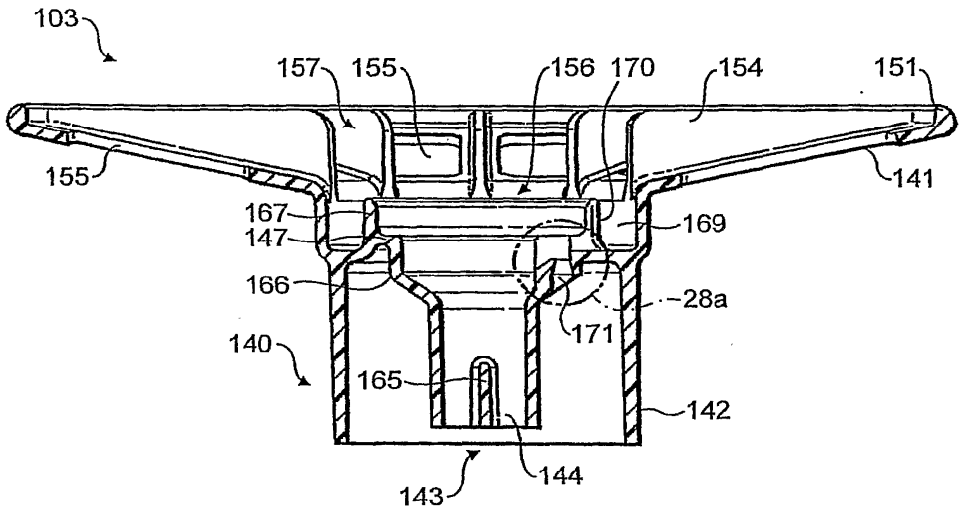


FIG. 28

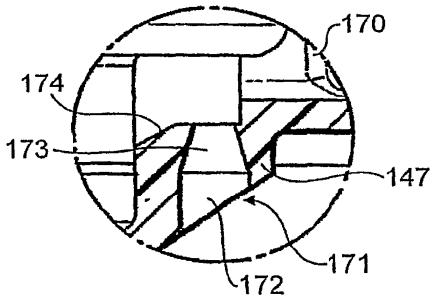


FIG. 28a

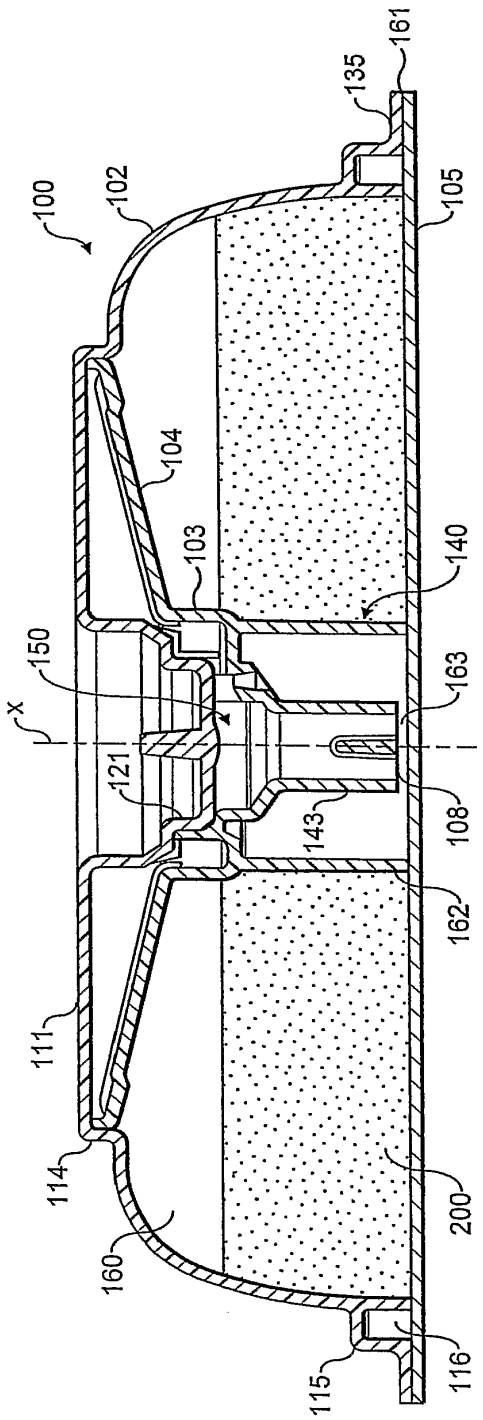

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FIG. 29

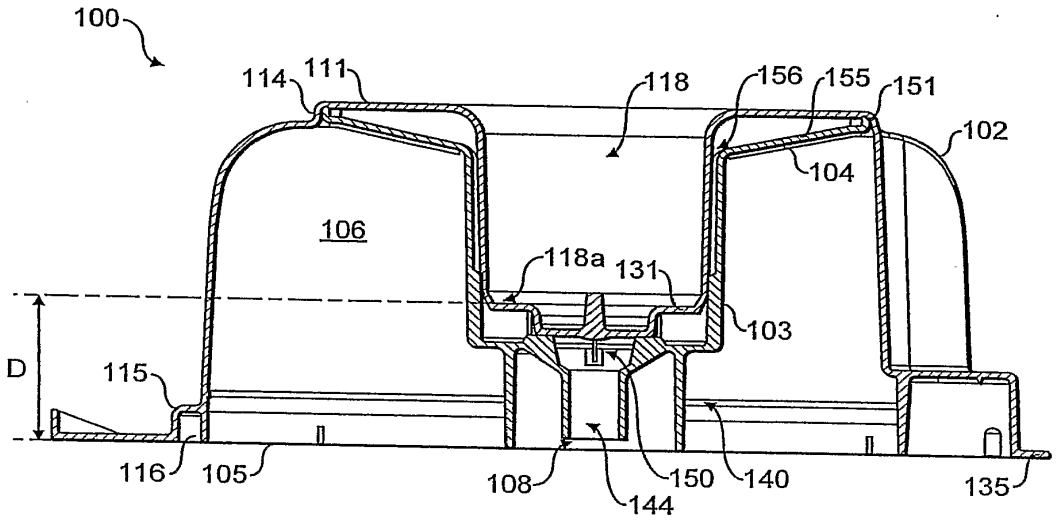

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FIG. 30

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000551

A. CLASSIFICATION OF SUBJECT MATTER
INV. A47J31/36 A47J31/06 A47J31/46
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A47J

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	GB 2 434 969 A (HALE ROBERT [CA]) 15 August 2007 (2007-08-15) paragraphs [0018] - [0037]; figures	1-4,6-12 21
X	US 6 405 637 B1 (CAI EDWARD Z [US]) 18 June 2002 (2002-06-18) column 3, line 23 - column 30, line 6; figures	1-4,6-12
X	WO 2004/098360 A1 (SALTON [US]; WINSTANLEY PETER [US]; ROSSI GIAMPIERO [IT]) 18 November 2004 (2004-11-18) page 4, line 14 - page 11, line 16; figures	1-4,6-12

-/--

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"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

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Date of the actual completion of the international search	Date of mailing of the international search report
1 July 2010	08/07/2010

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	De Terlizzi, Marino

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000551

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 440 644 A1 (KRAFT FOODS R & D INC [DE]) 28 July 2004 (2004-07-28) cited in the application paragraphs [0092] - [0094]; figures	1-4,6-12
X	EP 1 133 944 A2 (FIANARA INT BV [NL]) 19 September 2001 (2001-09-19)	1-4,6-12
A	paragraphs [0015] - [0032]; figures	20
X	EP 1 016 364 A2 (ANTICA TORREF DEL BORGO BARDAS [IT]) 5 July 2000 (2000-07-05)	1-4,6-12
A	paragraphs [0013] - [0061]; figures	20
X	EP 0 232 460 A2 (FELDMUEHLE AG [DE]) 19 August 1987 (1987-08-19) column 3, line 20 - column 4, line 34; figures	1-4,6-12
X	US 2007/056994 A1 (WOODNORTH DOUGLAS [US] ET AL) 15 March 2007 (2007-03-15) paragraphs [0018] - [0043]; figures	1-4,6-12
X	EP 0 781 520 A1 (BRAUN AG [DE]) 2 July 1997 (1997-07-02) column 7, line 53 - column 15, line 36; figures	1-4,6-12

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2010/000551

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		US 5778765 A	14-07-1998

Form PCT/ISA/210 (patent family annex) (April 2005)

Espacenet

WO2012057257A1 TRANSPARENT CONDUCTIVE GLASS SUBSTRATE

Applicants: FUJIKI HIRONAO [JP],HATORI HIROTAKA [JP],NISHIYAMA SAKAE [JP],NSC CO LTD [JP],SHINETSU POLYMER CO [JP],TAKEUCHI KAZUMA [JP],TANIGUCHI ATSUSHI [JP],YOSHIDA KAZUYOSHI [JP]

Inventors: FUJIKI HIRONAO [JP],HATORI HIROTAKA [JP],NISHIYAMA SAKAE [JP],TAKEUCHI KAZUMA [JP],TANIGUCHI ATSUSHI [JP],YOSHIDA KAZUYOSHI [JP]

Classifications:
IPC ***G02F1/1333; H01B13/00; H01B5/14;***

CPC **G02F1/00 (KR); G02F1/1333 (KR); G02F1/133305 (EP); H01B13/00 (KR); H01B5/00 (KR); H01B5/14 (KR);** G02F2202/022 (EP); G02F2202/09 (EP);

Priorities: JP2010244358A 2010-10-29

Application: WO2012057257A1·2011-10-27

Publication: WO2012057257A1·2012-05-03

Published as: **CN103189931A; CN103189931B; JP5888700B2; JPWO2012057257A1; KR101815337B1; KR20140015265A; SG190020A1; TW201222570A; TWI556263B;** WO2012057257A1

TRANSPARENT CONDUCTIVE GLASS SUBSTRATE

Abstract

[Problem] To provide a flexible transparent conductive glass substrate having flexibility similar to a plastic substrate, achieving hardness and transparency not found in plastics, and having adherence that can withstand use with a curved surface. [Solution] A transparent conductive glass substrate having a conductive polymer layer on at least one surface of a thin glass substrate, and having a surface resistance of 1.8 GO/sq or less, total light transmittance of 85% or greater, surface pencil hardness of H or greater, and no failure with bending of a radius of 25 mm is manufactured. Furthermore, a conductive polymer application forming the conductive polymer layer contains a conductive polymer and polyanions and also contains one or a plurality selected from a group that includes binders, curing agents, conductivity increasing agents, surface active agents, catalysts, and agents for improving adhesion.

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NESPRESSO USA, INC. v. K-FEE SYSTEM GMBH
IPR2023-00485, U.S. PATENT 11,230,430

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Notice

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DESCRIPTION WO2012057257A1

Transparent conductive glass substrate The present invention relates to a transparent conductive glass substrate.

A transparent conductive film obtained by sputtering a conductive ceramic such as ITO on a glass substrate is currently used in many electronic members. However, since ITO has problems of depletion of indium, which is a raw material, and soaring prices, alternatives to other conductive materials are required, and technically, it is flexible and has flexibility from the conventional hard substrate. Boards have been craving for design and functionality.

Therefore, attempts have been made to coat various plastics with a dispersion of metal nanoparticles, a transparent conductive polymer, or the like on a film base material (see, for example, Patent Document 1). ITO, which has been conventionally used for glass substrates, has no flexibility, and recently, the above conductive composition has been studied as an alternative to these. In the case of plastic sheets, for example, polyethylene terephthalate resins used in a wide range, it is common to provide a layer such as an "easy-adhesive layer" in order to apply these conductive compositions. This layer is provided to facilitate coating, improve the adhesion between the plastic sheet and the conductive material, and improve the quality and performance of the product, such as not containing air bubbles.

On the other hand, although ITO sputtering and dispersion coating are generally performed on a glass substrate as a transparent conductive material, these glasses are thick and inflexible molded bodies. A technique for applying a conductive polymer to glass using a slit coater is disclosed (see, for example, Patent Document 2). The glass used here does not have flexibility and is not used on a curved surface. Further, this conductive polymer is used by coating it on ITO as a hole injection layer of an organic EL, and the degree of adhesion to a glass substrate should be considered small.

However, a plastic base material as disclosed in Patent Document 1 has no problem in bending property and flexibility, but has problems such as warpage, hardness or scratch property, and deterioration of optical transparency, and is a hard coat. It was necessary to apply a material or the like as a base for the conductive layer.

Further, glass as disclosed in Patent Document 2 does not have flexibility and is not used on a curved surface, and a conductive polymer is used by coating it on ITO as a hole injection layer of an organic EL. Therefore, the degree of adhesion to the glass substrate should be considered small.

The present invention has been made in view of the above problems, and is flexible having the same flexibility as a plastics substrate, realizing hardness and transparency not found in plastics, and having adhesion that can withstand use on a curved surface. It is an object of the present invention to provide a transparent conductive glass substrate.

Such an object is achieved by the present invention of the following (1) to (15).

(1) It has a conductive polymer layer on at least one surface on a glass substrate, has a surface resistance of 1.8 GΩ / □ or less, a total light transmittance of 85% or more, a surface pencil hardness of H or more, and is not damaged by bending at R25 mm. A transparent conductive glass substrate characterized by.

(2) The conductive polymer coating material forming the conductive polymer layer is selected from the group containing a conductive polymer and a polyanion, and further containing a binder, a curing agent, a highly conductive agent, a surfactant, a catalyst and an adhesion improver. The transparent conductive glass substrate according to claim 1, further comprising one or more of the following.

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(3) The conductive polymer is an organic polymer whose main chain is composed of a π-conjugated system, such as polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylenes, polyanilines, polyacenes, and polythiophene vinylenes. The transparent conductive glass substrate according to claim 2, wherein the transparent conductive glass substrate comprises one or a plurality of polymers belonging to one or a plurality selected from the group containing the, and the copolymers thereof.

(4) The transparent conductive glass substrate according to claim 2 or 3, wherein the conductive polymer contains at least a polymer anion and a polymer of thiophene or a thiophene derivative.

(5) The transparent conductive glass substrate according to claim 4, wherein the polymer anion is polystyrene sulfonic acid, and the polymer of thiophene or a thiophene derivative is poly-3,4-ethylenedioxythiophene.

(6) The polyanion is one or more polymers having one or more anion groups selected from the group containing a monosubstituted sulfate group, a monosubstituted phosphate group, a phosphoric acid group, a carboxy group and a sulfo group. The transparent conductive glass substrate according to claim 2, wherein the transparent conductive glass substrate comprises.

(7) The binder is a binder resin, and the binder resin is a thermosetting resin and / or a thermoplastic resin that can be compatible with or mixed and dispersed with one or more conductive polymer paints. Item 2. The transparent conductive glass substrate according to Item 2.

(8) The high conductivity agent is a nitrogen-containing aromatic cyclic compound, a compound having two or more hydroxy groups, a compound having two or more carboxy groups, one or more hydroxy groups and one or more carboxys. One or more compounds selected from the group consisting of a compound having a group, a compound having an amide group, a compound having an imide group, a lactam compound, a compound having a glycidyl group, a silane coupling agent, DMSO and a water-soluble organic solvent. The transparent conductive glass substrate according to claim 2, wherein the transparent conductive glass substrate is characterized by the above.

(9) According to any one of claims 2 to 8, the conductive polymer coating material has a boiling point in the range of 50 to 200 ° C. and contains 5 to 95% by mass of a solvent soluble in water. The transparent conductive glass substrate according to the description.

(10) The conductive polymer layer according to claim 1 to 9, wherein the conductive polymer layer is produced through a process of drying and heating and / or irradiation of infrared rays or ultraviolet rays following application of the conductive polymer paint. The transparent conductive glass substrate according to any one of the items.

(11) The application of the conductive polymer paint is performed by a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, an inkjet printing method, a spin coating method, a die coating method including a slit coater method, a curtain coating method and a cap coating method. The transparent conductive glass substrate according to claim 10, wherein the process is performed by any method selected from the group including.

(12) The transparent conductive glass according to claim 1, wherein the thickness of the glass substrate is in the range of 0.03 to 0.7 mm, and the contact angle of the glass surface with water is in the range of 5 to 40 degrees. substrate.

(13) The transparent conductive glass substrate according to claim 1 or 12, wherein the surface of the glass substrate having at least the conductive polymer layer includes a portion formed by etching with a hydrofluoric acid-containing mixed solution. ..

(14) The transparent conductive glass substrate according to any one of claims 1 to 13, wherein the conductive polymer layer is cured by heating and / or irradiation with infrared rays or ultraviolet rays.

(15) The transparent conductive glass substrate according to any one of claims 1 to 14, wherein the conductive polymer layer is cured at a temperature of 160 ° C. or lower.

According to the present invention, it is possible to provide a flexible transparent conductive glass substrate which has the same flexibility as a plastics substrate, realizes hardness and transparency not found in plastics, and has adhesion that can withstand use on a curved surface. Can be done.

Hereinafter, a mode for carrying out the present invention (hereinafter, referred to as an embodiment).) Will be described in detail.

As a result of various studies to achieve the above object, the present inventors form a conductive polymer layer on a glass substrate having a thickness of 0.03 to 0.7 mm and an arithmetic mean roughness Ra of 0.2 μm or less. As a result, it was clarified that it is possible to manufacture a flexible transparent conductive glass substrate having the same flexibility as a plastics substrate, realizing hardness and transparency not found in plastics, and having adhesion that can withstand use on a curved surface.

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In order to achieve the object of the present invention, a flexible and strong glass substrate is first required. Therefore, it is desirable that the thickness of the glass substrate is in the range of 0.03 to 0.7 mm and the arithmetic average roughness Ra is 0.2 μm or less. If the thickness exceeds 0.7 mm, sufficient flexibility cannot be obtained, and if it is less than 0.03 mm, no strength is associated. Examples of the glass substrate include alkaline glass, nonionic glass, and quartz glass, and among these, nonionic glass can be preferably used from the viewpoint of environmental load.

Methods for producing thin film glass include chemical etching with hydrofluoric acid. Examples of the chemical used for chemical etching include a mixed solution of two or more kinds containing hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and hydrofluoric acid. Of these, hydrofluoric acid is preferably used from the viewpoint of glass slimming. As a condition for chemical etching, it is desirable that the liquid temperature is 25 to 55 degrees for the reason of slimming accuracy.

The glass substrate in the present invention is preferably thinned by chemical etching because the bending strength is inferior when there are grinding marks on the surface. Further, even glass thinned by grinding has an arithmetic mean roughness Ra of 0.2 μm or less, and those having improved wettability with a conductive polymer by treating the surface with hydrofluoric acid or the like are stronger due to the conductive polymer coating. It is possible to obtain a product that can be used more and more.

When applying a conductive polymer, the choice of conductive polymer is selected from polyaniline, polypyrrole, and polythiophene, but polythiophene is preferable from the viewpoint of transparency and color conductivity, and polyethylenedioxythiophene and polystyrene sulfone are preferable. Most preferably, it consists of a complex with an acid.

In this case, since the conductive polymer dispersion is dispersed in water or a solvent containing water, the glass substrate in the present invention preferably has a contact angle with water between 5 and 40 degrees, more preferably 5. It is between 7 degrees. If the contact angle exceeds 40 degrees, the conductive polymer dispersion solution causes cissing, and the coating film is not clean and the adhesion strength cannot be obtained.

As a method of applying the conductive polymer paint on a glass substrate, a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, an inkjet printing method, a spin coating method, a die coating method including a slit coater method, a curtain coating method, Examples include the cap coat method.

Since it is necessary to form a low resistance and highly transparent film with a thin film of 10 to 1000 nm, the conductive polymer is advantageous for forming a thin film, such as a gravure printing method, a flexographic printing method, an inkjet printing method, a spin coating method, and a die coating. It is preferable to apply by a method such as a method. Of these, the gravure printing method, the flexographic printing method, and the die coating method are preferable because they can easily handle a large area. Furthermore, the fast-drying solvent contained in the conductive polymer paint dries and solidifies during coating. It is desirable to use a die-coating method that facilitates ink supply in a closed system so that the amount does not fluctuate and foreign matter is not generated. In particular, if a slit coater is used in the die coating method, it is possible to coat a thin film uniformly, with less solvent drying, that is, less ink fluctuation during coating, and less loss of expensive conductive polymer paint.

A slit coater is a device that coats a thin film with a slot die that moves on a substrate in a non-contact manner. It has advantages such as.

As will be described later, the material of the wetted part needs to be a material resistant to corrosion because the conductive polymer solution often has strong acidity. For example, SUS-based metal is used, especially in SUS304. It is desirable from the viewpoint of acid resistance.

Under the coating conditions by the slit coater, it is important to control the nozzle gap, coating speed, work distance, coating flow rate, etc., and the nozzle gap is preferably 80 to 150 μm from the viewpoint of coating accuracy. If it is less than 80 μm, the entire coated surface becomes thin, and if it exceeds 150 μm, the entire coated surface becomes thick, so this range is appropriate.

From the viewpoint of coating accuracy, the coating speed is preferably 10 to 60 mm / sec, and preferably 20 to 50 mm / sec. If it is less than 10 mm / sec, the entire coated surface becomes thick, and if it exceeds 60 mm / sec, the entire coated surface becomes thin, so this range is appropriate.

The work distance is preferably 80 to 150 μm from the viewpoint of coating accuracy. If it is less than 80 μm, it becomes a thin film, and if it exceeds 150 μm, it becomes a thick film, so this range is appropriate.

From the viewpoint of thickness accuracy, the discharge flow rate is preferably 0.05 to 0.7 ml, and preferably 0.1 ml to 0.55 ml. If it is less than 0.05 ml, the central coating area of the head becomes thick, and if it exceeds 0.7 ml, the coating areas at both ends of the head become thick, so this range is appropriate.

The conductive polymer used in the present invention is not only a conductive polymer and a polyanion for dispersing in a dopant and a medium, but also a binder for solidifying and curing the conductive polymer composition, a curing agent, and a

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high level for improving conductivity. It may contain a conductive agent, a surfactant, a catalyst, an adhesion improver and the like.

The conductive polymer, polyanion, binder resin and highly conductive agent will be described in detail below.

(Conductive polymer) The conductive polymer can be used as long as it is an organic polymer whose main chain is composed of a π-conjugated system. Examples thereof include polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylenes, polyanilines, polyacenes, polythiophene vinylenes, and copolymers thereof. Polypyrroles, polythiophenes and polyanilines are preferable from the viewpoint of ease of polymerization and stability in air.

Specific examples of such a conductive polymer include polypyrrole, poly (3-methylpyrrole), poly (3-ethylpyrrole), poly (3-n-propylpyrrole), poly (3-butylpyrrole), and poly (3-butylpyrrole). 3-octylpyrrole), poly (3-decylpyrrole), poly (3-dodecylpyrrole), poly (3,4-dimethylpyrrole), poly (3,4-dibutylpyrrole), poly (3-carboxypyrrole), Poly (3-methyl-4-carboxypyrrole), poly (3-methyl-4-carboxyethylpyrrole), poly (3-methyl-4-carboxybutylpyrrole), poly (3-hydroxypyrrole), poly (3-hydroxypyrrole) Methoxypyrrole), poly (3-ethoxypyrrole), poly (3-butoxypyrrole), poly (3-hexyloxypyrrole), poly (3-methyl-4-hexyloxypyrrole), poly (3-methyl-4-Hexyloxypyrrole), poly (thiophene), poly (3-methylthiophene), poly (3-ethylthiophene), poly (3-propylthiophene), poly (3-butylthiophene), poly (3-hexylthiophene), Poly (3-heptylthiophene), poly (3-octylthiophene), poly (3-decylthiophene), poly (3-dodecylthiophene), poly (3-octadecylthiophene), poly (3-bromothiophene), poly (3-bromothiophene) 3-Chlorothiophene), poly (3-iodothiophene), poly (3-cyanothiophene), poly (3-phenylthiophene), poly (3,4-dimethylthiophene), poly (3,4-dibutylthiophene), Poly (3-hydroxythiophene), poly (3-methoxythiophene), poly (3-ethoxythiophene), poly (3-butoxythiophene), poly (3-hexyloxythiophene), poly (3-heptyloxythiophene), Poly (3-octyloxythiophene), poly (3-decyloxythiophene), poly (3-dodecyloxythiophene), poly (3-octadecyloxythiophene), poly (3,4-dihydroxythiophene), poly (3, 4-dimethoxythiophene), poly (3,4-diethoxythiophene), poly (3,4-dipropoxythiophene), poly (3,4-dibutoxythiophene), poly (3,4-dihexyloxythiophene), Poly (3,4-diheptyloxythiophene), poly (3,4-dioctyloxythiophene) , Poly (3,4-didecyloxythiophene), Poly (3,4-didodecyloxythiophene), Poly (3,4-ethylenedioxythiophene), Poly (3,4-propylenedioxythiophene) , Poly (3,4-butendioxythiophene), Poly (3-methyl-4-methoxythiophene), Poly (3-methyl-4-ethoxythiophene), Poly (3-carboxythiophene), Poly (3-methyl) -4-carboxythiophene), poly (3-methyl-4-carboxyethylthiophene), poly (3-methyl-4-carboxybutylthiophene), polyaniline, poly (2-methylaniline), poly (3-isobutylaniline) , Poly (2-aniline sulfonic acid), poly (3-aniline sulfonic acid) and the like.

Among them, one or two selected from polypyrrole, polythiophene, poly (N-methylpyrrole), poly (3-methylthiophene), poly (3-methoxythiophene), and poly (3,4-ethylenedioxythiophene). (Co) polymer is preferably used from the viewpoint of resistance value and reactivity. Furthermore, polypyrrole and poly (3,4-ethylenedioxythiophene) are more preferable because they have higher conductivity and improved heat resistance.

(Polyanion) The polyanion is a polymer that solubilizes a conductive polymer, and examples of the polyanion include a polymer having an anion group.

The anionic group of the polyanion may be a functional group capable of chemically oxidizing a conductive polymer, but from the viewpoint of ease of production and stability, a monosubstituted sulfate group and a monosubstituted phosphoric acid are used. Ester groups, phosphate groups, carboxy groups, sulfo groups and the like are preferable. Further, from the viewpoint of the doping effect of the functional group on the conductive polymer, a sulfo group, a monosubstituted sulfate group and a carboxy group are more preferable.

Specific examples of the polyanion include polyvinyl sulfonic acid, polystyrene sulfonic acid, polyallyl sulfonic acid, polyacrylic sulfonic acid, polymethacryl sulfonic acid, poly-2-acrylamide-2-methylpropane sulfonic acid, polyisoprene sulfonic acid, and polyvinyl carboxylic acid. Examples thereof include acids, polystyrene carboxylic acids, polyallyl carboxylic acids, polyacrylic carboxylic acids, polymethacryl carboxylic acids, poly-2-acrylamide-2-methylpropane carboxylic acids, polyisoprene carboxylic acids and polyacrylic acids. These homopolymers may be used, or two or more kinds of copolymers may be used.

Of these, polyvinyl sulfonic acid, polyacrylic sulfonic acid, polymethacryl sulfonic acid, and polystyrene sulfonic acid, which are excellent in thermal stability and dispersibility, are preferable, and polystyrene sulfonic acid is most preferable because good conductivity can be obtained.

The degree of polymerization of the polyanion is preferably in the range of 10 to 100,000 monomer units, and more preferably in the range of 50 to 10,000 from the viewpoint of solvent solubility and conductivity.

The content of the polyanion is preferably in the range of 0.1 to 10 mol, more preferably in the range of 1 to 7 mol, with respect to 1 mol of the conductive polymer. When the content of the polyanion is less than 0.1 mol, the doping effect on the conductive polymer tends to be weakened, and the conductivity may be insufficient. Moreover, the dispersibility and solubility in the solvent are lowered, and it becomes difficult to obtain a uniform dispersion liquid. Further, when the content of the polyanion is more than 10 mol, the content ratio of the conductive polymer is reduced, and it is also difficult to obtain sufficient conductivity.

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In order to produce a conductive polymer coating material, first, a polyanion component is dissolved in a solvent that dissolves the polyanionic component, a precursor monomer of the conductive polymer and a dopant, if necessary, are added, and the mixture is sufficiently stirred and mixed. Then, an oxidizing agent is added dropwise to the mixture thus obtained to proceed with polymerization to obtain a composite of a polyanion and a conductive polymer. Then, an oxidizing agent, a residual monomer, and a by-product are removed from the composite, purified, dissolved in an appropriate solvent, and if necessary, a dopant or a binder resin is added to obtain a conductive polymer coating material.

The solvent of the conductive polymer coating material is not particularly limited, and for example, water, N-methyl-2-pyrrolidone, N, N-dimethylformamide, N, N-dimethylacetamide, dimethylsulfoxide, hexamethylenephosphortriamide, acetonitrile, etc. Polar solvents such as benzonitrile, phenols such as cresol, phenol, xylenol, alcohols such as methanol, ethanol, propanol and butanol, ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, methyl acetate, ethyl acetate, propyl acetate, etc. Esters, hydrocarbons such as hexane, benzene, toluene, xylene, carboxylic acids such as formic acid and acetic acid, carbonate compounds such as ethylene carbonate and propylene carbonate, ether compounds such as dioxane and diethyl ether, ethylene glycol alkyl ether and propylene. Chain ethers such as glycol alkyl ether, polyethylene glycol alkyl ether, polypropylene glycol alkyl ether, heterocyclic compounds such as 3-methyl-2-oxazolidinone, acetonitrile, glutalogie nitrile, methoxy acetonitrile, propionitrile, benzonitrile and the like. Examples include nitrile compounds. These solvents may be used alone, as a mixture of two or more kinds, or as a mixture with other organic solvents.

As will be described later, the transparent conductive glass substrate of the present invention preferably has a surface molded by etching with hydrofluoric acid. Therefore, in order to improve the wettability to the surface, 5 mass of a solvent soluble in water is added. % Or more is preferable, and 10% by mass or more is more preferable. Here, "soluble in water" means that 1 g or more is dissolved in 100 g of water at 25 ° C.

This is because the above-mentioned composite of the conductive polymer and the polyanion is most stable as an aqueous solution because the polyanion exhibits water solubility, and it is desirable to select a solvent that is soluble in water. be. However, if the proportion of the solvent other than water is too large, the conductive polymer cannot be dispersed in the solution and the form as a paint cannot be maintained. Therefore, the solvent soluble in water is preferably 99% by mass or less, preferably 95% by mass. % Or less is desirable.

Further, as will be described later, the boiling point of the solvent is preferably 200 ° C. or lower, and preferably 180 ° C. or lower, because it is necessary to dry and cure the conductive polymer coating material at a low temperature. However, the boiling point of the solvent is preferably 50 ° C. or higher, more preferably 70 ° C. or higher, from the viewpoints of workability, leveling property, brushing prevention, etc. at the time of coating a slit-type coater or the like.

(Binder) Since the transparent conductive glass substrate of the present invention is used as an electrode or the like of a liquid crystal display or the like, it is necessary to cure it in the presence of various organic substances such as a liquid crystal material. Therefore, it is necessary to cure at a temperature of 120 ° C. or lower including evaporation of water or an organic solvent. As an example of such cross-linking, curing by irradiation with infrared rays, ultraviolet rays, etc., and heating is effective. In the case of curing by ultraviolet irradiation, curing can be achieved by adding a compound having a polyfunctional acrylic group, a sensitizer, and a photoinitiator. In the case of thermosetting, it is possible to immobilize the conductive polymer by adding a binder and curing it, and it is also possible to crosslink the polyanion. In order to cure at a temperature of 120 ° C. or lower in a relatively short time, a polyfunctional epoxy compound, a polyfunctional oxetane compound, a polyfunctional aziridine compound, etc. are used as a cross-linking agent, and a polymer carboxylic acid having high reactivity with these is used. It is recommended to use a curing catalyst. Further, a water-soluble or emulsified polyfunctional carbodiimide or the like can also be used.

[Binder resin] The conductive polymer paint preferably contains a binder resin because it enhances the environmental durability and scratch resistance of the coating film and improves the adhesion to the base material. Since the conductive polymer paint contains a binder resin, the pencil hardness (JIS K 5400) of the conductive polymer film formed from the conductive polymer paint is likely to be HB or higher. That is, the binder resin exerts a function as a hard coat component.

The binder resin may be a thermosetting resin or a thermoplastic resin as long as it can be compatible with or mixed and dispersed with the conductive polymer coating material. For example, polyesters such as polyethylene terephthalate, polybutylene terephthalate, and polyethylene naphthalate; polyimides such as polyimide and polyamideimide; polyamides such as polyamide 6, polyamide 6, 6, polyamide 12, and polyamide 11; polyvinylidene fluoride, polyvinyl fluoride, and poly. Fluororesin such as tetrafluoroethylene, ethylene tetrafluoroethylene copolymer, polychlorotrifluoroethylene; vinyl resin such as polyvinyl alcohol, polyvinyl ether, polyvinyl butyral, polyvinyl acetate, polyvinyl chloride; epoxy resin; oxetane resin; aziridine resin: Examples thereof include oxazoline resin: xylene resin; aramid resin; polyimide silicone; polyurethane; polyurea; melamine resin; phenol resin; polyether; acrylic resin and copolymers thereof.

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These binder resins may be dissolved in an organic solvent, may be made into an aqueous solution by adding a functional group such as a sulfo group or a carboxy group, or may be dispersed in water such as emulsified.

Further, the binder resin can be used by adding a curing agent such as a cross-linking agent and a polymerization initiator, a polymerization accelerator, a solvent, a viscosity modifier and the like, if necessary.

Among the binder resins, one or more of polyurethane, polyester, acrylic resin, polyamide, polyimide, epoxy resin, oxetane resin, aziridine resin, melamine resin, and polyimide silicone is preferable because they can be easily mixed. In addition, acrylic resin is suitable for applications such as glass substrates because it has high hardness and excellent transparency.

Further, the binder resin preferably contains a liquid polymer that is cured by thermal energy and / or light energy.

Here, examples of the liquid polymer that is cured by thermal energy include a reactive polymer and a self-crosslinked polymer.

The reactive polymer is a polymer obtained by polymerizing a monomer having a substituent, and examples of the substituent include a hydroxy group, a carboxy group, an acid anhydride, an oxetane group, a glycidyl group, and an amino group. Specific monomers include polyfunctional alcohols such as ethylene glycol, diethylene glycol, dipropylene glycol, and glycerin, malonic acid, succinic acid, glutamate, pimeric acid, ascorbic acid, phthalic acid, acetylsartyl acid, adipic acid, and isophthal. Carous acid compounds such as acids, benzoic acid and m-toluic acid, maleic anhydride, phthalic anhydride, succinic anhydride, dichloromaleic anhydride, tetrachlorophthalic anhydride, tetrahydrophthalic anhydride, pymellitic anhydride and the like. Oxetane compounds such as 3,3-dimethyloxetane, 3,3-dichloromethyloxetane, 3-methyl-3-hydroxymethyloxetane, azidomethylmethyloxetane, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, phenol novolac. Polyglycidyl ether, N, N-diglycidyl-p-aminophenol glycidyl ether, tetrabromobisphenol A diglycidyl ether, hydrogenated bisphenol A diglycidyl ether (ie, 2,2-bis (4-glycidyloxycyclohexyl) propane), Neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylpropanpolyglycidyl ether, hexahydrophthalic acid diglycidyl ether, propylene glycol diglycidyl ether, tripropylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether , Fatty acid modified epoxy, diethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerin polyglycidyl ether, diglycerin polyglycidyl ether, polyglycerin polyglycidyl ether, sorbitol polyglycidyl ether, ethylene oxide lauryl alcohol glycidyl ether, ethylene oxidephenol glycidyl ether, Glycidyl ether compounds such as glycidyl ether adipate, N, N-diglycidyl aniline, tetraglycidyl diaminodiphenylmethane, N, N, N, N-tetraglycidyl-m-xylylene diamine, triglycidyl isocyanurate, N, N-diglycidyl Glycidylamine compounds such as -5,5-dialkylhydrantiin, diethylenetriamine, triethylenetetramine, dimethylaminopropylamine, N-aminoether Lupiperazin, benzyldimethylamine, tris (dimethylaminomethyl) phenol, DHP30-tri (2-ethylhexoate), metaphenylenediamine, diaminodiphenylmethane, diaminodiphenylsulfone, dicyandiamide, boron trifluoride, monoethylamine, methanediamine, Among amine compounds such as xylene diamine and ethyl methyl imidazole, compounds containing two or more oxylan rings in one molecule, glycidyl compounds based on epichlorohydrin of bisphenol A, or similar compounds thereof can be mentioned.

In the reactive polymer, a cross-linking agent, a catalyst, a cationic polymerization initiator described later, or the like may be used in combination. Examples of the cross-linking agent include melamine resin, epoxy resin, metal oxide and the like. Examples of the metal oxide include the basic metal compounds Al (OH) 3, Al (OOC · CH3) 2 (OOCH), Al (OOC · CH3) 2, ZrO (OCH3), Mg (OOC · CH3), Ca (OH) 2, Ba (OH) 3, and the like can be used as appropriate.

The self-crosslinking polymer is one in which functional groups are self-crosslinked by heating, and examples thereof include those containing a glycidyl group and a carboxy group, and those containing both an N-methylol and a carboxy group.

Examples of the liquid polymer cured by light energy include oligomers or prepolymers such as polyester, epoxy resin, oxetane resin, polyacrylic, polyurethane, polyimide, polyamide, polyamideimide, and polyimide silicone.

Examples of the monomer unit constituting the liquid polymer cured by light energy include bisphenol A / ethylene oxide-modified diacrylate, dipentaerythritol hexa (penta) acrylate, dipentaerythritol monohydroxypentaacrylate, and dipropylene glycol di. Acrylate, trimethylolpropane triacrylate, glycerin propoxytriacrylate, 4-hydroxybutyl acrylate, 1,6-hexanediol diacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, isobornyl acrylate, polyethylene glycol diacrylate, Acrylates such as pentaerythritol triacrylate, tetrahydrofurfuryl acrylate, trimethylpropan triacrylate, tripropylene glycol diacrylate, tetraethylene glycol dimethacrylate, alkyl methacrylate, allyl methacrylate, 1,3-butylene glycol dimethacrylate, n-butyl Methacrylate, benzyl methacrylate, cyclohexyl methacrylate, diethylene glycol dimethacrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate, 1,6-hexanediol dimethacrylate, 2-hydroxyethyl methacrylate, isobornyl methacrylate, lauryl methacrylate, phenoxyethyl methacrylate, t-butyl Methacrylates such as methacrylate, tetrahydrofurfuryl methacrylate, trimethylolpropane trimethacrylate, allyl glycidyl ether, butyl glycidyl ether, higher alcohol glycidyl edel, 1,6-hexanediol glycidyl ether, phenyl glycidyl ether, glycidyl ether such as stearyl glycidyl ether. Kind, diacetone acrylamide, N, N-dimethylacrylamide, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylate, methacrylicamide, N-methylolacrylamide, N, N-dimethylacrylamide, acryloylmorpholine, N-vinylformamide, N-methyl Acrylate such as acrylamide, N-isopropylacrylamide, Nt-butylacrylamide, N-phenylacrylamide, acryloyl piperidine, 2-hydroxyethyl acrylamide, etc. Methacyl) amides, 2-chloroethyl vinyl ethers, cyclohexyl vinyl ethers, ethyl vinyl

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ethers, hydroxybutyl vinyl ethers, isobutyl vinyl ethers, triethylene glycol vinyl ethers and other vinyl ethers, vinyl butyrate, monomerochloroacetate vinyl, vinyl pivalate and other carboxylic acid vinyl esters. Examples thereof include monofunctional monomers and polyfunctional monomers.

The liquid polymer that is cured by light energy is cured by the photopolymerization initiator. Examples of the photopolymerization initiator include acetophenones, benzophenones, Michler benzoylbenzoates, α-amyloxime esters, tetramethylthiuram monosulfide, and thioxanthones. Further, as a photosensitizer, n-butylamine, triethylamine, tri-n-butylphosphine and the like can be mixed.

Examples of the cationic polymerization initiator include aryldiazonium salts, diarylhalonium salts, triphenylsulfonium salts, silanol / aluminum chelates, α-sulfonyloxyketones and the like.

The content of the binder resin is 1 to 1000% by mass, preferably 10 to 400% by mass, based on 100% by mass of the total of the conductive polymer and the polyanion. If the content of the binder resin is less than 1% by mass, the durability of the conductive polymer layer may be insufficient, and if it exceeds 1000% by mass, the content of the conductive polymer in the conductive polymer layer decreases. , Sufficient conductivity cannot be obtained.

(Highly conductive agent) The highly conductive agent is a component that improves the conductivity of the conductive coating film formed from the conductive polymer solution.

Specifically, the highly conductive agent is a nitrogen-containing aromatic cyclic compound, a compound having two or more hydroxy groups, a compound having two or more carboxy groups, one or more hydroxy groups, and one or more hydroxy groups. At least one compound selected from the group consisting of a compound having a carboxy group, a compound having an amide group, a compound having an imide group, a lactam compound, a compound having a glycidyl group, a silane coupling agent, DMSO, and a water-soluble organic solvent. be.

[Nitrogen-containing aromatic cyclic compounds] Examples of the nitrogen-containing aromatic cyclic compounds include pyridines and their derivatives containing one nitrogen atom, imidazoles containing two nitrogen atoms and their derivatives, and pyrimidines. Classes and derivatives thereof, pyrimidines and derivatives thereof, triazines containing three nitrogen atoms and derivatives thereof, and the like. From the viewpoint of solvent solubility and the like, pyridines and their derivatives, imidazoles and their derivatives, pyrimidines and their derivatives are preferable.

Specific examples of pyridines and their derivatives include pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 4-ethylpyridine, N-vinylpyridine, 2,4-dimethylpyridine, 2,4. , 6-trimethylpyridine, 3-cyano-5-methylpyridine, 2-pyridinecarboxylic acid, 6-methyl-2-pyridinecarboxylic acid, 4-pyridinecarboxyaldehyde, 4-aminopyridine, 2,3-diaminopyridine, 2 , 6-Diaminopyridine, 2,6-diamino-4-methylpyridine, 4-hydroxypyridine, 4-pyridinemethanol, 2,6-dihydroxypyridine, 2,6-pyridinedimethanol, methyl 6-hydroxynicotinate, 2, -Hydridine-5-pyridinemethanol, ethyl 6-hydroxynicotinate, 4-pyridinemethanol, 4-pyridineethanol, 2-phenylpyridine, 3-methylquinoline, 3-ethylquinolin, quinolinol, 2,3-cyclopentenopyridine , 2,3-Cyclohexanopyridine, 1,2-di (4-pyridyl) ethane, 1,2-di (4-pyridyl) propane, 2-pyridinecarboxyaldehyde, 2-pyridinecarboxylic acid, 2-pyridinecarbonitrile , 2,3-Pyridine dicarboxylic acid, 2,4-Pyridine dicarboxylic acid, 2,5-Pyridine dicarboxylic acid, 2,6-Pyridine dicarboxylic acid, 3-Pyridine sulfonic acid and the like.

Specific examples of imidazoles and derivatives thereof include imidazole, 2-methylimidazole, 2-propyl imidazole, 2-undylulmidazole, 2-phenylimidazole, N-methylimidazole, N-vinyl imidazole, and N-allyl imidazole. , 1- (2-Hydroxyethyl) imidazole (N-hydroxyethyl imidazole), 2-ethyl-4-methylimidazole, 1,2-dimethylimidazole, 1-benzyl-2-methylimidazole, 1-benzyl-2-phenyl Imidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, 1-acetylimidazole, 4,5-imidazole dicarboxylic acid, 4 , 5-Imidazole Dicarboxylate dimethyl, benzimidazole, 2-aminovenes imidazole, 2-aminobenzimidazole-2-sulfonic acid, 2-amino-1-methylvenes imidazole, 2-hydroxyvens imidazole, 2- (2-Pyridyl) Bends imidazole and the like can be mentioned.

Specific examples of pyrimidines and their derivatives include 2-amino-4-chloro-6-methylpyrimidine, 2-amino-6-chloro-4-methoxypyrimidine, 2-amino-4,6-dichloropyrimidine, 2-Amino-4,6-dihydroxypyrimidine, 2-amino-4,6-dimethylpyrimidine, 2-amino-4,6-dimethoxypyrimidine, 2-aminopyrimidine, 2-amino-4-methylpyrimidine, 4,6 -Dihydroxypyrimidine, 2,4-dihydroxypyrimidine-5-carboxylic acid, 2,4,6-triaminopyrimidine, 2,4-dimethoxypyrimidine, 2,4,5-trihydroxypyrimidine, 2,4-pyrimidinediol, etc. Can be mentioned.

Specific examples of pyrazines and their derivatives include pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine, pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid, 5-methylpyrazinecarboxylic acid, pyrazineamide, 5 -Methylpyrazine amide, 2-cyanopyrazine, aminopyrazine, 3-aminopyrazine-2-carboxylic acid, 2-ethyl-3-methylpyrazine, 2,3-dimethylpyrazine, 2,3-diethylpyrazine and the like can be mentioned.

Specific examples of triazines and their derivatives include 1,3,5-triazine, 2-amino-1,3,5-triazine, 3-amino-1,2,4-triazine, and 2,4-diamino. -6-Phenyl-1,3,5-triazine, 2,4,6-triamino-1,3,5-triazine, 2,4,6-tris (trifluoromethyl) -1,3,5-triazine, 2,4,6-tri-2-pyridine-

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1,3,5-triazine, 3- (2-pyridine) -5,6-bis (4-phenylsulfonic acid) -1,2,4-triazine disodium , 3- (2-pyridine) -5,6-diphenyl-1,2,4-triazine, 3- (2-pyridine) -5,6-diphenyl-1,2,4-triazine-p, p'- Examples thereof include disodium disulfonate, 2-hydroxy-4,6-dichloro-1,3,5-triazine.

The content of the nitrogen-containing aromatic cyclic compound is preferably in the range of 0.1 to 100 mol, more preferably in the range of 0.5 to 30 mol, with respect to 1 mol of the anion group unit of the polyanion. Preferably, from the viewpoint of physical properties and conductivity of the conductive coating film, the range of 1 to 10 mol is particularly preferable. When the content of the nitrogen-containing aromatic cyclic compound is less than 0.1 mol, the interaction between the nitrogen-containing aromatic cyclic compound and the polyanion and the conjugated conductive polymer tends to be weakened, and the conductivity tends to be weakened. May run short. Further, when the nitrogen-containing aromatic cyclic compound is contained in an amount of more than 100 mol, the content of the conjugated conductive polymer is reduced, and it is also difficult to obtain sufficient conductivity.

[Compounds having 2 or more hydroxy groups] Examples of compounds having 2 or more hydroxy groups include propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, D-glucose, D-glucitol, and the like. Isoprene glycol, dimethylol propionic acid, butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol , Polyvalent aliphatic alcohols such as thiodiethanol, glucose, tartaric acid, D-glucaric acid, glutaconic acid; high molecular weight alcohols such as cellulose, polysaccharides, sugar alcohols; 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 2,3-Dihydroxy-1-pentadecylbenzene, 2,4-dihydroxyacetophenone, 2,5-dihydroxyacetophenone, 2,4-dihydroxybenzophenone, 2,6-dihydroxybenzophenone, 3,4-dihydroxybenzophenone, 3,5 -Dihydroxybenzophenone, 2,4'-dihydroxydiphenylsulphon, 2,2', 5,5'-tetrahydroxydiphenylsulphon, 3,3', 5,5'-tetramethyl-4,4'-dihydroxydiphenylsulphon, Hydroxyquinone carboxylic acid and its salts, 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 1, 4-Hydroquinone sulfonic acid and its salts, 4,5-hydroxybenzene-1,3-disulfonic acid and its salts, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,7 -Dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid, 1,6-dihydroxynaphthalene-2,5-dicarboxylic acid, 1,5-dihydroxynaphthoic acid, 1,4 -Dihydroxy-2-naphthoic acid phenyl ester, 4,5-dihydroxynaphthalene-2,7-disulfonic acid and its salts, 1,8-dihydroxy-3,6-naphthalenedisulfonic acid and its salts, 6,7-dihydroxy- 2-Naphthalene sulfonic acid and its salts, 1,2,3-trihydroxybenzene (pyrogaro) , 1,2,4-trihydroxybenzene, 5-methyl-1,2,3-trihydroxybenzene, 5-ethyl-1,2,3-trihydroxybenzene, 5-propyl-1,2, 3-Trihydroxybenzene, trihydroxybenzoic acid, trihydroxyacetophenone, trihydroxybenzophenone, trihydroxybenzoaldehyde, trihydroxyanthraquinone, 2,4,6-trihydroxybenzene, tetrahydroxy-p-benzoquinone, tetrahydroxyanthraquinone, garlic Examples include aromatic compounds such as methyl acid (methyl benzene) and ethyl garlic (ethyl benzene), potassium hydroquinone sulfonate and the like.

The content of the compound having two or more hydroxy groups is preferably in the range of 0.05 to 50 mol, preferably in the range of 0.3 to 10 mol, with respect to 1 mol of the anion group unit of the polyanion. More preferred. If the content of the compound having two or more hydroxy groups is less than 0.05 mol with respect to 1 mol of the anion group unit of the polyanion, the conductivity and heat resistance may be insufficient. Further, when the content of the compound having two or more hydroxy groups is more than 50 mol with respect to 1 mol of the anion group unit of the polyanion, the content of the π-conjugated conductive polymer in the conductive coating film is small. As a result, it is difficult to obtain sufficient conductivity.

[Compounds having 2 or more carboxy groups] Examples of compounds having 2 or more carboxy groups include maleic acid, fumaric acid, itaconic acid, citraconic acid, malonic acid, 1,4-butandicarboxylic acid, succinic acid and tartrate acid. , Adipic acid, D-glucaric acid, glutaconic acid, citric acid and other aliphatic carboxylic acids; phthalic acid, terephthalic acid, isophthalic acid, tetrahydrophthalic anhydride, 5-sulfoisophthalic acid, 5-hydroxyisophthalic acid, methyltetrahydro At least one in the aromatic ring, such as phthalic anhydride, 4,4'-oxydiphthalic acid, biphenyltetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, naphthalenedicarboxylic acid, trimellitic acid, pyromellitic acid, etc. Aromatic carboxylic acid compounds to which the above carboxy groups are bonded; examples thereof include digiycolic acid, oxydibutyric acid, thiodiacetic acid (thiodiacetic acid), thiodibutyric acid, iminodiacetic acid, iminobutyric acid and the like.

The compound having two or more carboxy groups is preferably in the range of 0.1 to 30 mol, more preferably in the range of 0.3 to 10 mol, with respect to 1 mol of the anion group unit of the polyanion. If the content of the compound having two or more carboxy groups is less than 0.1 mol with respect to 1 mol of the anion group unit of the polyanion, the conductivity and heat resistance may be insufficient. Further, when the content of the compound having two or more carboxy groups is more than 30 mol with respect to 1 mol of the anion group unit of the polyanion, the content of the π-conjugated conductive polymer in the conductive coating film is reduced. After all, it is difficult to obtain sufficient conductivity, and the physical properties of the conductive coating film may change.

[Compound having one or more hydroxy groups and one or more carboxy groups] Examples of the compound having one or more hydroxy groups and one or more carboxy groups include tartaric acid, glyceric acid, dimethylolbutanoic acid, and dimethylolpropane. Acids, D-glucaric acid, glutaconic acid and the like can be mentioned.

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The content of the compound having one or more hydroxy groups and one or more carboxy groups is preferably 1 to 5000 parts by mass with respect to 100 parts by mass in total of the polyanion and the π-conjugated conductive polymer. More preferably, it is up to 500 parts by mass. If the content of the compound having one or more hydroxy groups and one or more carboxy groups is less than 1 part by mass, the conductivity and heat resistance may be insufficient. Further, when the content of the compound having one or more hydroxy groups and one or more carboxy groups is more than 5000 parts by mass, the content of the π-conjugated conductive polymer in the conductive coating film is reduced, which is also the case. It is difficult to obtain sufficient conductivity.

[Amid compound] The compound having an amide group is a monomolecular compound having an amide bond in the molecule represented by -CO-NH- (the CO portion is a double bond). That is, examples of the amide compound include a compound having functional groups at both ends of the bond, a compound in which a cyclic compound is bonded to one end of the bond, and urea and a urea derivative in which the functional groups at both ends are hydrogen. And so on.

Specific examples of the amide compound include acetamide, malonamide, succinamide, maleamide, fumalamide, benzamide, naphthamide, phthalamide, isophthalamide, terephthalamide, nicotine amide, isonicotine amide, 2-fluamide, formamide, N-methylformamide and propionamide. , Propiolamide, Butylamide, Isobutylamide, Methacrylate, Palmitoamide, Stearylamide, Oleamide, Oxamide, Glutalamide, Adipamide, Sinnamamide, Glycolamide, Lactoamide, Glyceramide, Tartaramide, Citramide, Glyoxylamide, Pyrvoamide, Acetacetamide, Dimethyl Acetamide, benzylamide, anthranilamide, ethylenediaminetetraacetamide, diacetamide, triacetamide, dibenzamide, tribenzamide, rodanine, urea, 1-acetyl-2-thiourea, biuret, butylurea, dibutylurea, 1,3-dimethyl Examples thereof include urea, 1,3-diethylurea and derivatives thereof.

In addition, acrylamide can also be used as the amide compound. Examples of acrylamide include N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide, N, N-dimethylacrylamide, N, N-dimethylmethacrylate, N, N-diethylacrylamide, N, Examples thereof include N-diethylmethacrylate, 2-hydroxyethylacrylamide, 2-hydroxyethylmethacrylate, N-methylolacrylamide, and N-methylolmethacrylate.

The molecular weight of the amide compound is preferably 46 to 10000, more preferably 46 to 5000, and particularly preferably 46 to 1000.

The content of the amide compound is preferably 1 to 5000 parts by mass, more preferably 50 to 500 parts by mass, based on 100 parts by mass of the total of the polyanion and the π-conjugated conductive polymer. If the content of the amide compound is less than 1 part by mass, the conductivity and heat resistance may be insufficient. Further, when the content of the amide compound is more than 5000 parts by mass, the content of the π-conjugated conductive polymer in the conductive coating film is reduced, and it is also difficult to obtain sufficient conductivity.

[Imid compound] The amide compound is a single molecule compound having an imide bond (hereinafter referred to as an imide compound) because it has higher conductivity.) Is preferable. Examples of the imide compound include phthalimide and phthalimide derivatives, succinimide and succinimide derivatives, benzimide and benzimide derivatives, maleimide and maleimide derivatives, naphthalimide and naphthalimide derivatives, and the like.

Further, the imide compound is classified into an aliphatic imide, an aromatic imide and the like according to the type of the functional group at both ends, and the aliphatic imide is preferable from the viewpoint of solubility.

Further, the aliphatic imide compound is classified into a saturated aliphatic imide compound having an unsaturated bond between carbons in the molecule and an unsaturated aliphatic imide compound having an unsaturated bond between carbons in the molecule.

The saturated aliphatic imide compound is a compound represented by R1-CO-NH-CO-R2, and both R1 and R2 are saturated hydrocarbons. Specifically, cyclohexane-1,2-dicarboxyimide, allantin, hydantoin, barbituric acid, alloxan, glutarimide, succinimide, 5-butylhydantoinic acid, 5,5-dimethylhydantoin, 1-methylhydantoin, 1,5 , 5-trimethyl hydantoin, 5-hydantoin acetic acid, N-hydroxy-5-norbornene-2,3-dicarboxyimide, semicarbadide, α, α-dimethyl-6-methylsuccinimide, bis [2-(succinimideoxycarbonyloxy) Ethyl] sulfone, α-methyl-α-propylsuccinimide, cyclohexylimide and the like can be mentioned.

The unsaturated aliphatic imide compound is a compound represented by R1-CO-NH-CO-R2, and is a compound in which one or both of R1 and R2 have one or more unsaturated bonds. Specific examples include 1,3-dipropylene urea, maleimide, N-methylmaleimide, N-ethylmaleimide, N-hydroxymaleimide, 1,4-bismaleimidebutane, 1,6-bismaleimidehexane, and 1,8-bis. Maleimide octane, N-carboxyheptyl maleimide and the like can be mentioned.

The molecular weight of the imide compound is preferably 60 to 5000, more preferably 70 to 1000, and particularly preferably 80 to 500.

The content of the imide compound is preferably 10 to 10000 parts by mass, and more preferably 50 to 5000 parts by mass with respect to 100 parts by mass of the total of the π-conjugated conductive polymer and the polyanion. If the amount of the amide

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compound and the imide compound added is less than the lower limit, the effect of adding the amide compound and the imide compound is reduced, which is not preferable. Further, if the upper limit value is exceeded, the conductivity is lowered due to the decrease in the concentration of the π-conjugated conductive polymer, which is not preferable.

[Lactam compound] A lactam compound is an intramolecular cyclic amide of an aminocarboxylic acid, and a part of the ring is -CO-NR- (R is hydrogen or an arbitrary substituent). However, one or more carbon atoms in the ring may be replaced by unsaturated or heteroatoms. Examples of the lactam compound include pentano-4-lactam, 4-pentane lactam-5-methyl-2-pyrrolidone, 5-methyl-2-pyrrolidinone, hexano-6-lactam, 6-hexane lactam and the like.

The content of the lactam compound is preferably 10 to 10000 parts by mass, and more preferably 50 to 5000 parts by mass with respect to 100 parts by mass of the total of the π-conjugated conductive polymer and the polyanion. If the amount of the lactam compound added is less than the lower limit, the effect of adding the lactam compound is reduced, which is not preferable. Further, if the upper limit value is exceeded, the conductivity is lowered due to the decrease in the concentration of the π-conjugated conductive polymer, which is not preferable.

[Compounds having a glycidyl group] Examples of compounds having a glycidyl group include ethyl glycidyl ether, butyl glycidyl ether, t-butyl glycidyl ether, allyl glycidyl ether, benzyl glycidyl ether, glycidyl phenyl ether, bisphenol A, and diglycidyl ether. Examples thereof include glycidyl compounds such as glycidyl ether acrylate and glycidyl methacrylate ether.

The content of the compound having a glycidyl group is preferably 10 to 10000 parts by mass, and more preferably 50 to 5000 parts by mass with respect to 100 parts by mass of the total of the π-conjugated conductive polymer and the polyanion. If the amount of the compound having a glycidyl group added is less than the lower limit, the effect of adding the compound having a glycidyl group is reduced, which is not preferable. Further, if the upper limit value is exceeded, the conductivity is lowered due to the decrease in the concentration of the π-conjugated conductive polymer, which is not preferable.

[Silane Coupling Agent] Specific examples of the silane coupling agent include vinyl trichlorosilane, vinyl trimethoxysilane, vinyl triethoxysilane, 2- (3,4-epylcyclohexyl) ethyltrimethoxysilane, and 3-glycidoxy. Propyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 3-glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane , 3-methacryloxypropylmethyldiethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, N-2- (aminoethyl) -3-aminopropylmethyldimethoxysilane, N-2- (Aminoethyl) -3-aminopropyltriethoxysilane, N-2- (aminoethyl) -3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxy Hydrochloride of Cyril-N- (1,3-dimethyl-butylidene) propylamine, N-phenyl-3-aminopropyltrimethoxysilane, N- (vinylbenzyl) -2-aminoethyl-3-aminopropyltrimethoxysilane , 3-Ureidopropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltrimethoxysilane, bis (triethoxysilylpropyl) tetrasulfide, 3-isocyanuppropyltriethoxysilane And so on.

The content of the silane coupling agent can be added in any amount as needed, and is not particularly limited. It is preferably 10 to 10000 parts by mass with respect to 100 parts by mass in total of the π-conjugated conductive polymer and the polyanion.

Hereinafter, Examples 1 to 4 and Comparative Examples 1 to 3 according to the present invention will be described with reference to Table 1.

(Preparation of materials) [1] Preparation of polystyrene sulfonic acid 1.14 g of ammonium persulfate dissolved in 10 ml of water in advance while dissolving 206 g of sodium styrene sulfonate in 1000 ml of ion-exchanged water and stirring at 80 ° C. The agent solution was added dropwise for 20 minutes and the solution was stirred for 2 hours. 1000 ml of sulfuric acid diluted to 10% by mass and 10000 ml of ion-exchanged water were added to the resulting sodium styrene sulfonate-containing solution, and about 10000 ml of the polystyrene sulfonic acid-containing solution was removed using an ultrafiltration method. , 10000 ml of ion-exchanged water was added to the residual liquid, and about 10000 ml of the solution was removed by using an ultrafiltration method. The above ultrafiltration operation was repeated 3 times. Further, about 10,000 ml of ion-exchanged water was added to the obtained filtrate, and about 10,000 ml of the solution was removed by using an ultrafiltration method. This ultrafiltration operation was repeated 3 times. The ultrafiltration conditions are as follows. Fractional molecular weight of ultrafiltration membrane: 30,000 Cross-flow type Supply liquid flow rate: 3000 ml / min Membrane partial pressure: 0.12 Pa Water in the obtained solution is removed under reduced pressure to obtain colorless solid polystyrene sulfonic acid. rice field.

[2] Preparation of polystyrene sulfonic acid-doped poly (3,4-ethylenedioxythiophene) aqueous solution 14.2 g of 3,4-ethylenedioxythiophene and 36.7 g of polystyrene sulfonic acid obtained in [1] were added to 2000 ml. The solution dissolved in ion-exchanged water was mixed at 20 ° C. The mixed solution thus obtained was kept at 20 ° C., and while stirring, 29.64 g of ammonium persulfate dissolved in 200 ml of ion-exchanged water and 8.0 g of a ferric sulfate oxidation catalyst solution were slowly added. The reaction was carried out with stirring for 3 hours. 2000 ml of ion-exchanged water was added to the obtained reaction solution, and about 2000 ml of the solution was removed using an ultrafiltration method. This operation was repeated 3 times. Then, 200 ml of sulfuric acid diluted to 10% by mass and 2000 ml of ion-exchanged water were added to the treated solution subjected to the above filtration treatment, and about 2000 ml of the treated solution was removed using an

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ultrafiltration method, and 2000 ml of the treated solution was removed. Ion-exchanged water was added and about 2000 ml of liquid was removed using an ultrafiltration method. This operation was repeated 3 times. Further, 2000 ml of ion-exchanged water was added to the obtained treatment liquid, and about 2000 ml of the treatment liquid was removed by using an ultrafiltration method. This operation was repeated 5 times to obtain an aqueous solution of about 1.5% by mass of blue polystyrene sulfonate-doped poly (3,4-ethylenedioxythiophene) (PEDOT-PSS). The ultrafiltration conditions are the same as in [1].

[3] Preparation of glass substrate A glass substrate was prepared by chemical etching (liquid temperature 38 to 42 ° C.) while bubbling nonionic glass using a mixed solution of hydrofluoric acid, hydrochloric acid, and nitric acid. The thickness of this glass substrate was 0.4 mm, the water contact angle on the surface was 6.2 degrees, and the arithmetic mean roughness Ra was 0.0008 μm.

[4] Preparation of glass substrate A glass substrate was prepared by chemical etching (liquid temperature 38 to 42 ° C.) while bubbling nonionic glass using a blower. The thickness of this glass substrate was 0.4 mm, the water contact angle on the surface was 6.2 degrees, and the arithmetic mean roughness Ra was 0.195 μm.

[5] Preparation of glass substrate A glass substrate was prepared by chemical etching (liquid temperature 38 to 42 ° C.) while bubbling nonionic glass using a blower. The thickness of this glass substrate was 2 mm, the water contact angle on the surface was 6.2 degrees, and the arithmetic mean roughness Ra was 0.0008 μm.

(Measurement and evaluation) (Arithmetic mean roughness Ra) Measured according to JIS B 0601-2001.

(Surface resistance value) Measured according to JIS K 7194 using Loresta MCP-T600 manufactured by Mitsubishi Chemical Corporation.

(Light transmittance) The light transmittance was measured according to JIS K7136 using a haze meter measuring device (NDH5000) manufactured by Nippon Denshoku Kogyo Co., Ltd.

(Pencil hardness) Using a test pencil specified in JIS S6006, the hardness at which no scratches were observed under a load of 750 g was measured according to JIS K5600.

The (flexible) transparent conductive glass substrate was wound around a cylinder having a radius (R) of 25 mm so as to be in contact with the cylinder by 180 degrees, and then unwound 5 times, and the change in the surface resistance value before and after that was measured.

(Example 1) In 600 g of the PEDOT-PSS aqueous solution obtained in [2], 3.6 g of methyl garlic acid, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals), 20 g of dimethyl sulfoxide, 2.5 g of hydroxyacrylate, 7.2 g of pentaerythritol triacrylate and 300 g of ethanol were mixed and stirred to obtain a conductive polymer solution A.

Using a slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC, on one surface of the glass substrate obtained from the conductive polymer solution A in [3], nozzle gap 150 μm, coating speed 20 mm / sec, work distance 100 μm, It is applied with a discharge flow rate of 0.11 ml, dried at 100 ° C. for 2 minutes by infrared irradiation, and then irradiated with ultraviolet rays (high-pressure mercury lamp 120W, 500mJ / cm2, 178mW / cm2) and cured to form a conductive coating film. rice field. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured by the following methods.

(Example 2) In 600 g of the PEDOT-PSS aqueous solution obtained in [2], 3.6 g of methyl garlicate, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals), 20 g of dimethyl sulfoxide, and diethylene glycol diglycidyl ether 9. 2 g, 0.2 g of 2-methylimidazole, 250 g of ethanol, and 50 g of ethylene glycol were mixed and stirred to obtain a conductive polymer solution B. Using a slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC, on one surface of the glass substrate obtained from the conductive polymer solution B in [3], nozzle gap 150 μm, coating speed 40 mm / sec, work distance 100 μm, The coating was applied at a discharge rate of 0.3 ml, dried at 120 ° C. for 2 minutes by infrared irradiation and cured to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

(Example 3) 600 g of PEDOT-PSS aqueous solution (Krebios PH1000: manufactured by Stark), 3.6 g of methyl garlic acid, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals), 20 g of dimethyl sulfoxide, diethylene glycol diglycidyl ether. 9.2 g, 0.2 g of 2-methylimidazole, 0.5 g of garlic acid, 250 g of ethanol, and 50 g of ethylene glycol were mixed and stirred to obtain a conductive polymer solution C. Using a slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC, on one surface of the glass substrate obtained from the conductive polymer solution C in [3], nozzle gap 130 μm, coating speed 40 mm / sec, work distance 100 μm, The coating was applied at a discharge rate of 0.21 ml, dried at 120 ° C. for 2 minutes by infrared irradiation and cured to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

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(Example 4) A slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC was used on one surface of the glass substrate obtained by obtaining the conductive polymer solution C in [4], and the nozzle gap was 130 μm and the coating speed was 60 mm / sec. , The work distance was 80 μm, the discharge flow rate was 0.6 ml, and the mixture was dried and cured by infrared irradiation at 120 ° C. for 2 minutes to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

(Example 5) To 500 g of the PEDOT-PSS aqueous solution obtained in [2], 2 g of 2-methylimidazole, 150 g of water-dispersible polyester resin (Byronal MD1480: solid content 25% by mass), 3.6 g of garlic acid, 20 g of dimethylsulfoxide. , 1500 g of methanol was mixed and stirred to obtain a conductive polymer solution D. A slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC, was used on one surface of the glass substrate obtained by obtaining this conductive polymer solution D in [3], and the nozzle gap was 150 μm, the coating speed was 40 mm / sec, and the work distance was 100 μm. , And dried at 120 ° C. for 2 minutes by infrared irradiation to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

(Comparative Example 1) An ITO film was formed by sputtering on one surface of the glass substrate obtained in [3] to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

(Comparative Example 2) An ITO film was formed by sputtering on one surface of the glass substrate obtained in [4] to form a conductive coating film. The surface resistance and light transmittance of the conductive coating film, the pencil hardness, and the flexibility of the transparent conductive glass substrate were measured.

(Comparative Example 3) A slit coater manufactured by INNEXT Co., Ltd., model number IS-7900IL-NSC was used on one surface of the glass substrate obtained by obtaining the conductive polymer solution C in [5], and the nozzle gap was 130 μm and the coating speed was 60 mm / sec. When the coating was applied at a work distance of 80 μm and a discharge flow rate of 0.6 ml, the surface resistance, light transmittance and pencil hardness of the conductive coating film could not be measured, and the sample was damaged in the flexibility measurement of the transparent conductive glass substrate.

Table 1 compares the results of Examples 1 to 4 and Comparative Examples 1 to 3.

Although the present invention has been described above using the embodiments, it goes without saying that the technical scope of the present invention is not limited to the scope described in the above embodiments.

It will be apparent to those skilled in the art that various changes or improvements can be made to the above embodiments. Further, it is clear from the description of the scope of claims that the form to which such a modification or improvement is added may be included in the technical scope of the present invention.

The transparent conductive glass substrate of the present invention is used as a glass substrate material for VA liquid crystal display, TN liquid crystal display, IPS liquid crystal display and the like, and is used for preventing liquid crystal surface charging that hinders the viewing angle of the liquid crystal drive electrode and IPS. For the reason of production yield, the transparent conductive glass substrate used for these may be coated with a conductive polymer after enclosing the liquid crystal first. In this case, since the liquid crystal material is a heat-sensitive organic material, the liquid crystal material In order to prevent heat denaturation, the temperature for drying and curing the conductive polymer layer is preferably 200 ° C. or lower, and preferably 160 ° C. or lower. Conventionally, the ITO film formation is carried out in a high vacuum environment. Therefore, if the liquid crystal is sealed before the ITO film formation, the liquid crystal expands under reduced pressure and the glass is broken. The transparent conductive film made of a conductive polymer does not require a reduced pressure environment such as a high vacuum, and can be constructed at normal pressure, so that it has an advantage that it is not destroyed in a vacuum.

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CLAIMS WO2012057257A1

1.

It has a conductive polymer layer on at least one surface on a glass substrate, has a surface resistance of 1.8 GΩ / □ or less, a total light transmittance of 85% or more, a surface pencil hardness of H or more, and is not damaged by bending R25 mm. Transparent conductive glass substrate.

2.

The conductive polymer coating material forming the conductive polymer layer is selected from the group containing a conductive polymer and a polyanion, and further containing a binder, a curing agent, a highly conductive agent, a surfactant, a catalyst and an adhesion improver. The transparent conductive glass substrate according to claim 1, further comprising one or more.

3.

The conductive polymer is an organic polymer whose main chain is composed of a π-conjugated system, such as polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylenes, polyanilines, polyacenes, polythiophene vinylenes, and The transparent conductive glass substrate according to claim 2, wherein the transparent conductive glass substrate comprises one or more polymers belonging to one or more selected from the group containing those copolymers.

4.

The transparent conductive glass substrate according to claim 2 or 3, wherein the conductive polymer contains at least a polymer anion and a polymer of thiophene or a thiophene derivative.

5.

The transparent conductive glass substrate according to claim 4, wherein the polymer anion is polystyrene sulfonic acid, and the polymer of the thiophene or thiophene derivative is poly-3,4-ethylenedioxythiophene.

6.

The polyanion comprises one or more polymers having one or more anion groups selected from the group containing monosubstituted sulfate group, monosubstituted phosphate group, phosphate group, carboxy group and sulfo group. The transparent conductive glass substrate according to claim 2, wherein the transparent conductive glass substrate.

7.

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The binder is a binder resin, and the binder resin is a thermosetting resin and / or a thermoplastic resin that is compatible with or can be mixed and dispersed with the conductive polymer coating material. Item 2. The transparent conductive glass substrate according to Item 2.

8.

The highly conductive agent comprises a nitrogen-containing aromatic cyclic compound, a compound having two or more hydroxy groups, a compound having two or more carboxy groups, one or more hydroxy groups, and one or more carboxy groups. One or more compounds selected from the group consisting of a compound having a compound, a compound having an amide group, a compound having an imide group, a lactam compound, a compound having a glycidyl group, a silane coupling agent, DMSO and a water-soluble organic solvent. The transparent conductive glass substrate according to claim 2.

9.

The invention according to any one of claims 2 to 8, wherein the conductive polymer coating material has a boiling point in the range of 50 to 200 ° C. and contains 5 to 95% by mass of a solvent soluble in water. Transparent conductive glass substrate.

10.

Any of claims 1 to 9, wherein the conductive polymer layer is produced by a step of drying and heating and / or irradiation of infrared rays or ultraviolet rays following the application of the conductive polymer paint. The transparent conductive glass substrate according to Item 1.

11.

The coating of the conductive polymer coating material includes a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, an inkjet printing method, a spin coating method, a die coating method including a slit coater method, a curtain coating method and a cap coating method. The transparent conductive glass substrate according to claim 10, wherein the process is performed by any method selected from the group.

12.

The transparent conductive glass substrate according to claim 1, wherein the thickness of the glass substrate is in the range of 0.03 to 0.7 mm, and the contact angle of the glass surface with water is in the range of 5 to 40 degrees.

13.

The transparent conductive glass substrate according to claim 1 or 12, wherein at least the surface of the glass substrate having the conductive polymer layer includes a portion formed by etching with a hydrofluoric acid-containing mixed solution.

14.

The transparent conductive glass substrate according to any one of claims 1 to 13, wherein the conductive polymer layer is cured by heating and / or irradiation with infrared rays or ultraviolet rays.

15.

The transparent conductive glass substrate according to any one of claims 1 to 14, wherein the conductive polymer layer is cured at a temperature of 160 ° C. or lower.

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(54) **Title**: TRANSPARENT CONDUCTIVE GLASS SUBSTRATE

(54) 発明の名称 : 透明導電ガラス基板

(57) **Abstract**: [Problem] To provide a flexible transparent conductive glass substrate having flexibility similar to a plastic substrate, achieving hardness and transparency not found in plastics, and having adherence that can withstand use with a curved surface. [Solution] A transparent conductive glass substrate having a conductive polymer layer on at least one surface of a thin glass substrate, and having a surface resistance of 1.8 GΩ/sq or less, total light transmittance of 85% or greater, surface pencil hardness of H or greater, and no failure with bending of a radius of 25 mm is manufactured. Furthermore, a conductive polymer application forming the conductive polymer layer contains a conductive polymer and polyanions and also contains one or a plurality selected from a group that includes binders, curing agents, conductivity increasing agents, surface active agents, catalysts, and agents for improving adhesion.

(57) 要約: 【課題】プラスチックス基板と同様の柔軟性を持ち、且つプラスチックスにはない硬さと透明度を実現し曲面での使用に耐えうる密着性を有するフレキシブルな透明導電ガラス基板を提供する。【解決手段】 薄いガラス基板上の少なくとも一面に導電性ポリマー層を有し、表面抵抗が１．８ＧΩ／□以下、全光線透過率が８５％以上、表面鉛筆硬度Ｈ以上で、Ｒ ２５ｍｍの折り曲げで破損しない透明導電ガラス基板を製造する。また、導電性ポリマー層を形成する導電性ポリマー塗料が、導電性ポリマー及びポリアニオンを含み、さらにバインダ、硬化剤、高導電化剤、界面活性剤、触媒及び接着性向上剤を含む群から選択される１つ又は複数を含む。

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明　細　書

発明の名称 ： 透明導電ガラス基板

技術分野

［0001］　本発明は、透明導電ガラス基板に関する。

背景技術

［0002］　ガラス基材にＩＴＯなど導電性セラミックスをスパッタリングした透明導電性膜は現在多くの電子部材に使用されている。しかしながら、ＩＴＯには原材料であるインジウムの枯渇、価格高騰問題が存在するため、他の導電材料への代替が求められており、又技術的には従来の固い基板からフレキシブル性を持った柔軟な基板がデザインや機能の面から渇望されてきている。

［0003］　このため、フィルム基材に金属ナノ粒子の分散体、また透明導電性ポリマーなどを種々のプラスチックスに塗工することが試みられている（例えば、特許文献１参照）。従来ガラス基板に用いられてきたＩＴＯは可撓性が無く近来はこれらに代わるものとして上記導電性組成物が検討されている。プラスチックスシート例えば広範囲に用いられるポリエチレンテレフタレート樹脂などの場合、これらの導電性組成物を塗工する為に多くの場合「易接着層」といった層を設けることが一般的である。この層は塗工を容易にし、またプラスチックスシートと導電性材料との密着性を向上させたり、気泡を含ませない等、商品としての品位や性能を向上させるために設けられる。

［0004］　一方、ガラス基板に透明導電材料としてＩＴＯのスパッタリングや分散体の塗工が一般的に行われているがこれらのガラスは厚みが厚く柔軟性のない成型体である。導電性ポリマーをガラスにスリットコーターを用いて塗布する技術が開示されている（例えば、特許文献２参照）。ここで用いられているガラスはフレキシビリティーを有するものではなく曲面で用いられることもない。又、この導電性ポリマーは、有機ＥＬの正孔注入層としてＩＴＯ上に塗布して用いられておりガラス基板との密着性については考慮すべき度合いが小さい。

先行技術文献

特許文献

[0005] 特許文献1：特開２００８－２８８０６７号公報

特許文献2：特開２００４－１３９８１４号公報

発明の概要

発明が解決しようとする課題

[0006] しかしながら、特許文献１に開示されているようなプラスチックス基材では、折り曲げ性や柔軟性に問題は無いものの反りや硬さ或いは擦傷性、光学透過性が劣化することなどに問題がありハードコート材料などを導電層の下地として塗工する必要があった。

[0007] 又、特許文献２に開示されているようなガラスはフレキシビリティーを有するものではなく曲面で用いられることもなく、導電性ポリマーは、有機ＥＬの正孔注入層としてＩＴＯ上に塗布して用いられておりガラス基板との密着性については考慮すべき度合いが小さい。

[0008] 本発明は上記問題点に鑑みなされたものであって、プラスチックス基板と同様の柔軟性を持ち、且つプラスチックスにはない硬さと透明度を実現し曲面での使用に耐えうる密着性を有するフレキシブルな透明導電ガラス基板を提供することを目的とする。

課題を解決するための手段

[0009] このような目的は、下記（１）～（１５）の本発明により達成される。

[0010] （１）ガラス基板上の少なくとも一面に導電性ポリマー層を有し、表面抵抗が１．８ＧΩ／□以下、全光線透過率が８５％以上、表面鉛筆硬度Ｈ以上、Ｒ

２５ｍｍの折り曲げで破損しないことを特徴とする透明導電ガラス基板。

[0011] （２）導電性ポリマー層を形成する導電性ポリマー塗料が、導電性ポリマー及びポリアニオンを含み、さらにバインダ、硬化剤、高導電化剤、界面活性剤、触媒及び接着性向上剤を含む群から選択される１つ又は複数を含むこ

とを特徴とする請求項１に記載の透明導電ガラス基板。

[0012] （３）導電性ポリマーは、主鎖がπ共役系で構成されている有機高分子である、ポリピロール類、ポリチオフェン類、ポリアセチレン類、ポリフェニレン類、ポリフェニレンビニレン類、ポリアニリン類、ポリアセン類、ポリチオフェンビニレン類、及びそれらの共重合体を含む群から選択される１つ又は複数に属する１つ又は複数のポリマーからなることを特徴とする請求項２に記載の透明導電ガラス基板。

[0013] （４）導電性ポリマーは、少なくともポリマーアニオンとチオフェンまたはチオフェン誘導体のポリマーとを含むことを特徴とする請求項２又は３に記載の透明導電ガラス基板。

[0014] （５）ポリマーアニオンはポリスチレンスルホン酸であり、チオフェンまたはチオフェン誘導体のポリマーはポリ－３，４－エチレンジオキシチオフェンであることを特徴とする請求項４に記載の透明導電ガラス基板。

[0015] （６）ポリアニオンは、一置換硫酸エステル基、一置換リン酸エステル基、リン酸基、カルボキシ基及びスルホ基を含む群から選択される１つ又は複数のアニオン基を有する１つ又は複数のポリマーを含むことを特徴とする請求項２に記載の透明導電ガラス基板。

[0016] （７）バインダはバインダ樹脂であり、バインダ樹脂が、１つ又は複数の、導電性ポリマー塗料と相溶又は混合分散可能な熱硬化性樹脂及び／又は熱可塑性樹脂であることを特徴とする請求項２に記載の透明導電ガラス基板。

[0017] （８）高導電化剤は、窒素含有芳香族性環式化合物、２個以上のヒドロキシ基を有する化合物、２個以上のカルボキシ基を有する化合物、１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物、アミド基を有する化合物、イミド基を有する化合物、ラクタム化合物、グリシジル基を有する化合物、シランカップリング剤、ＤＭＳＯ及び水溶性有機溶媒からなる群より選択される１つ又は複数の化合物であることを特徴とする請求項２に記載の透明導電ガラス基板。

[0018] （９）導電性ポリマー塗料は、沸点が５０～２００℃の範囲であり且つ水

に可溶の溶剤を５～９５質量％含むことを特徴とする特許請求項２～８のいずれか１項に記載の透明導電ガラス基板。

[0019] （１０）導電性ポリマー層は、導電性ポリマー塗料の塗布に続き、乾燥及び加熱並びに／又は赤外線もしくは紫外線の照射の工程を経て作製されたものであることを特徴とする請求項１～９のいずれか１項に記載の透明導電ガラス基板。

[0020] （１１）導電性ポリマー塗料の塗布は、スクリーン印刷法、グラビア印刷法、フレキソ印刷法、オフセット印刷法、インクジェット印刷法、スピンコート法、スリットコーター法を含むダイコート法、カーテンコート法及びキャップコート法を含む群から選択されるいずれかの方法によって行うことを特徴とする請求項１０に記載の透明導電ガラス基板。

[0021] （１２）ガラス基板の厚みが０．０３～０．７ｍｍの範囲にあり、ガラス表面の水に対する接触角が５～４０度の範囲にあることを特徴とする請求項１に記載の透明導電ガラス基板。

[0022] （１３）ガラス基板上の少なくとも導電性ポリマー層を有する面がフッ化水素酸含有混合液によるエッチングによって成形された部位を含むものであることを特徴とする請求項１又は１２に記載の透明導電ガラス基板。

[0023] （１４）導電性ポリマー層は、加熱及び/又は赤外線もしくは紫外線の照射によって硬化されたものであることを特徴とする請求項１～１３のいずれか１項に記載の透明導電ガラス基板。

[0024] （１５）導電性ポリマー層は１６０℃以下の温度で硬化されてなることを特徴とする請求項１～１４のいずれか１項に記載の透明導電ガラス基板。

発明の効果

[0025] 本発明によれば、プラスチックス基板と同様の柔軟性を持ち、且つプラスチックスにはない硬さと透明度を実現し曲面での使用に耐えうる密着性を有するフレキシブルな透明導電ガラス基板を提供することができる。

発明を実施するための形態

[0026] 以下、本発明を実施するための形態（以下、実施形態という。）について

詳細に説明する。

[0027] 本発明者らは、上記目的を達成するために種々検討した結果、厚み０．０３～０．７ｍｍ、算術平均粗さＲａが０．２μｍ以下のガラス基板上に、導電性ポリマー層を形成することにより、プラスチックス基板と同様の柔軟性を持ち、且つプラスチックスにはない硬さと透明度を実現し曲面での使用に耐えうる密着性を有するフレキシブルな透明導電ガラス基板を製造できることを究明した。

[0028] 本発明の目的を達成するためには、まず柔軟性があり、且つ強度のあるガラス基板が必要である。このためガラス基板の厚みは ０．０３～０．７ｍｍの範囲にあり、算術平均粗さＲａが０．２μｍ以下であることが望ましい。厚みが０．７ｍｍを超える場合には十分な屈曲性が得られず０．０３ｍｍ未満である場合には強度が伴わない。ガラス基板は、材質としてアルカリガラス、ノニオンガラス、石英ガラスなどが挙げられるが、このうち、環境負荷の観点からノニオンガラスが好ましく使用できる。

[0029] 薄膜ガラスの製造方法にはフッ酸によるケミカルエッチング等がある。ケミカルエッチングに使用する薬品としては塩酸、硫酸、硝酸、リン酸とフッ酸を含む２種以上の混合液が挙げられる。このうち、ガラススリミングの観点からフッ酸が好ましく使用される。ケミカルエッチングの条件として、スリミング精度の理由から液温２５～５５度であることが望ましい。

[0030] 表面に研削痕がある場合には曲げ強度が劣ることなどから、本発明におけるガラス基板は化学エッチングで薄化したものが好ましい。また、研削によって薄化したガラスでも算術平均粗さＲａが０．２μｍ以下であり、表面をフッ酸などで処理することによって導電性ポリマーとの濡れ性を改善したものは導電性ポリマー被膜により強度が増し使用可能な製品を得ることができる。

[0031] 導電性ポリマーを塗布する場合に於いて、導電性ポリマーの選択肢はポリアニリン、ポリピロール、ポリチオフェン系から選択されるが、透明度及び色調導電性の観点からポリチオフェン系が望ましく更にはポリエチレンジオ

キシチオフェンとポリスチレンスルフォン酸との錯体からなるものが最も好ましい。

[0032] この場合導電性ポリマー分散体は水若しくは水を含んだ溶媒に分散されているため、本発明におけるガラス基板は水との接触角が５～４０度の間にあることが好ましく、より好ましくは５～７度の間である。接触角が４０度を超えると導電性ポリマー分散体溶液はハジキを起こし綺麗な塗膜にならず密着強度も得られない。

[0033] 導電性ポリマー塗料をガラス基板上に塗布する方法として、スクリーン印刷法、グラビア印刷法、フレキソ印刷法、オフセット印刷法、インクジェット印刷法、スピンコート法、スリットコーター法を含むダイコート法、カーテンコート法、キャップコート法などの方法が挙げられる。

[0034] 導電性ポリマーは、１０～１０００ｎｍといった薄膜で低抵抗かつ高透明な膜を形成する必要があることから、薄膜の形成に有利なグラビア印刷法、フレキソ印刷法、インクジェット印刷法、スピンコート法、ダイコート法などの方法で塗布することが好ましい。このうち、大面積にも対応しやすいことから、グラビア印刷法、フレキソ印刷法、ダイコート法が好ましく、さらにいえば、導電性ポリマー塗料に含まれる乾燥の速い溶媒が、塗布中に乾燥して固形分が変動したり、異物が発生しないように密閉系でのインク供給が容易なダイコート法が望ましい。

特に、ダイコート法の中でもスリットコーターを用いれば、薄膜を均一に、溶媒乾燥が少なく、すなわち塗工中のインク変動が少なく、また高価な導電性ポリマー塗料のロスも少ないコーティングが可能になる。

[0035] スリットコーターとは、基板上を非接触で動くスロットダイにより薄膜を塗工する装置であり、スピンコーターに比べ、材料の消費が少なく、タクトタイムの短縮が可能、フリンジの裏面への回り込みが無いなどの利点を有する。

[0036] 接液部の材質は、後述するように、導電性ポリマー溶液が強い酸性を有することが多いことから腐食に強い材質とすることが必要であり、たとえば、

ＳＵＳ系金属が用いられ、特にＳＵＳ３０４であることが耐酸性の観点から望ましい。

[0037] スリットコーターによるコーティング条件では、ノズルギャップ、塗布速度、ワークディスタンス、塗出流量等のコントロールが重要であり、ノズルギャップは塗布精度の観点から、８０～１５０μmであることが好ましい。８０μｍ未満であると塗工面全体が薄くなり、１５０μｍを超えると塗工面全体が厚くなることからこの範囲が適切である。

[0038] 塗付速度は塗布精度の観点から、１０～６０ｍｍ／ｓｅｃであることが好ましく、２０～５０ｍｍ／ｓｅｃであることが望ましい。１０ｍｍ／sec未満であると塗工面全体が厚くなり、６０ｍｍ／ｓｅｃを超えると塗工面全体が薄くなることからこの範囲が適切である。

[0039] ワークディスタンスは塗布精度の観点から、８０～１５０μｍであることが好ましい。８０μｍ未満であると薄膜となり、１５０μｍを超えると厚膜となることからこの範囲が適切である。

[0040] 吐出流量は厚みの精度の観点から、０．０５～０．７ｍｌであることが好ましく、　０．１ｍｌ～０．５５ｍｌであることが望ましい。０．０５ｍｌ未満であるとヘッドの中央塗工場所が厚くなり、０．７ｍｌを超えるとヘッドの両端の塗工場所が厚くなることからこの範囲が適切である。

[0041] 本発明に用いられる導電性ポリマーは導電性ポリマーとドーパント兼媒体に分散させるためのポリアニオン以外に、導電性ポリマー組成物を固化、硬化させるためのバインダ、硬化剤、導電性を向上させるための高導電化剤、界面活性剤、触媒、接着性向上剤などを含んでも良い。

[0042] 以下に、導電性ポリマー、ポリアニオン、バインダ樹脂及び高導電化剤について詳細に説明する。

[0043] （導電性ポリマー）

導電性ポリマーは、主鎖がπ共役系で構成されている有機高分子であれば使用できる。例えば、ポリピロール類、ポリチオフェン類、ポリアセチレン類、ポリフェニレン類、ポリフェニレンビニレン類、ポリアニリン類、ポリ

アセン類、ポリチオフェンビニレン類、及びこれらの共重合体等が挙げられる。重合の容易さ、空気中での安定性の点からは、ポリピロール類、ポリチオフェン類及びポリアニリン類が好ましい。

[0044] このような導電性ポリマーの具体例としては、ポリピロール、ポリ（３－メチルピロール）、ポリ（３－エチルピロール）、ポリ（３－ｎ－プロピルピロール）、ポリ（３－ブチルピロール）、ポリ（３－オクチルピロール）、ポリ（３－デシルピロール）、ポリ（３－ドデシルピロール）、ポリ（３，４－ジメチルピロール）、ポリ（３，４－ジブチルピロール）、ポリ（３－カルボキシピロール）、ポリ（３－メチル－４－カルボキシピロール）、ポリ（３－メチル－４－カルボキシエチルピロ―ル）、ポリ（３－メチル－４－カルボキシブチルピロール）、ポリ（３－ヒドロキシピロール）、ポリ（３－メトキシピロール）、ポリ（３－エトキシピロール）、ポリ（３－ブトキシピロール）、ポリ（３－ヘキシルオキシピロール）、ポリ（３－メチル－４－ヘキシルオキシピロール）、ポリ（３－メチル－４－ヘキシルオキシピロール）、ポリ（チオフェン）、ポリ（３－メチルチオフェン）、ポリ（３－エチルチオフェン）、ポリ（３－プロピルチオフェン）、ポリ（３－ブチルチオフェン）、ポリ（３－ヘキシルチオフェン）、ポリ（３－ヘプチルチオフェン）、ポリ（３－オクチルチオフェン）、ポリ（３－デシルチオフェン）、ポリ（３－ドデシルチオフェン）、ポリ（３－オクタデシルチオフェン）、ポリ（３－ブロモチオフェン）、ポリ（３－クロロチオフェン）、ポリ（３－ヨ―ドチオフェン）、ポリ（３－シアノチオフェン）、ポリ（３－フェニルチオフェン）、ポリ（３，４－ジメチルチオフェン）、ポリ（３，４－ジブチルチオフェン）、ポリ（３－ヒドロキシチオフェン）、ポリ（３－メトキシチオフェン）、ポリ（３－エトキシチオフェン）、ポリ（３－ブトキシチオフェン）、ポリ（３－ヘキシルオキシチオフェン）、ポリ（３－ヘプチルオキシチオフェン）、ポリ（３－オクチルオキシチオフェン）、ポリ（３－デシルオキシチオフェン）、ポリ（３－ドデシルオキシチオフェン）、ポリ（３－オクタデシルオキシチオフェン）、ポリ（３，４－ジヒ

ドロキシチオフェン）、ポリ（３，４－ジメトキシチオフェン）、ポリ（３，４－ジエトキシチオフェン）、ポリ（３，４－ジプロポキシチオフェン）、ポリ（３，４－ジブトキシチオフェン）、ポリ（３，４－ジヘキシルオキシチオフェン）、ポリ（３，４－ジヘプチルオキシチオフェン）、ポリ（３，４－ジオクチルオキシチオフェン）、ポリ（３，４－ジデシルオキシチオフェン）、ポリ（３，４－ジドデシルオキシチオフェン）、ポリ（３，４－エチレンジオキシチオフェン）、ポリ（３，４－プロピレンジオキシチオフェン）、ポリ（３，４－ブテンジオキシチオフェン）、ポリ（３－メチル－４－メトキシチオフェン）、ポリ（３－メチル－４－エトキシチオフェン）、ポリ（３－カルボキシチオフェン）、ポリ（３－メチル－４－カルボキシチオフェン）、ポリ（３－メチル－４－カルボキシエチルチオフェン）、ポリ（３－メチル－４－カルボキシブチルチオフェン）、ポリアニリン、ポリ（２－メチルアニリン）、ポリ（３－イソブチルアニリン）、ポリ（２－アニリンスルホン酸）、ポリ（３－アニリンスルホン酸）等が挙げられる。

[0045] 中でも、ポリピロール、ポリチオフェン、ポリ（Ｎ－メチルピロール）、ポリ（３－メチルチオフェン）、ポリ（３－メトキシチオフェン）、ポリ（３，４－エチレンジオキシチオフェン）から選ばれる１種又は２種からなる（共）重合体が抵抗値、反応性の点から好適に用いられる。さらには、ポリピロール、ポリ（３，４－エチレンジオキシチオフェン）は、導電性がより高い上に、耐熱性が向上する点から、より好ましい。

[0046] （ポリアニオン）

ポリアニオンとは、導電性ポリマーを可溶化する高分子であり、ポリアニオンとしては、アニオン基を有する高分子が挙げられる。

[0047] ポリアニオンのアニオン基としては、導電性ポリマーへの化学酸化ドープが起こりうる官能基であればよいが、中でも、製造の容易さ及び安定性の観点からは、一置換硫酸エステル基、一置換リン酸エステル基、リン酸基、カルボキシ基、スルホ基等が好ましい。さらに、官能基の導電性ポリマーへのドープ効果の観点より、スルホ基、一置換硫酸エステル基、カルボキシ基が

より好ましい。

[0048] ポリアニオンの具体例としては、ポリビニルスルホン酸、ポリスチレンスルホン酸、ポリアリルスルホン酸、ポリアクリルスルホン酸、ポリメタクリルスルホン酸、ポリー２ーアクリルアミドー２ーメチルプロパンスルホン酸、ポリイソプレンスルホン酸、ポリビニルカルボン酸、ポリスチレンカルボン酸、ポリアリルカルボン酸、ポリアクリルカルボン酸、ポリメタクリルカルボン酸、ポリー２ーアクリルアミドー２ーメチルプロパンカルボン酸、ポリイソプレンカルボン酸、ポリアクリル酸等が挙げられる。これらの単独重合体であってもよいし、２種以上の共重合体であってもよい。

[0049] これらのうち、熱安定性、分散性に優れるポリビニルスルホン酸、ポリアクリルスルホン酸、ポリメタクリルスルホン酸、ポリスチレンスルホン酸が好ましく、中でもポリスチレンスルホン酸は良好な導電性を得られることからもっとも好ましい。

[0050] ポリアニオンの重合度は、モノマー単位が１０～１０００００個の範囲であることが好ましく、溶媒溶解性及び導電性の点からは、５０～１００００個の範囲がより好ましい。

[0051] ポリアニオンの含有量は、導電性ポリマー１モルに対して０．１～１０モルの範囲であることが好ましく、１～７モルの範囲であることがより好ましい。ポリアニオンの含有量が０．１モルより少なくなると、導電性ポリマーへのドーピング効果が弱くなる傾向にあり、導電性が不足することがある。その上、溶媒への分散性及び溶解性が低くなり、均一な分散液を得ることが困難になる。また、ポリアニオンの含有量が１０モルより多くなると、導電性ポリマーの含有割合が少なくなり、やはり充分な導電性が得られにくい。

[0052] 導電性ポリマー塗料を製造するには、まず、ポリアニオン成分を、これを溶解する溶媒に溶解し、導電性ポリマーの前駆体モノマーと必要に応じてドーパントとを加えて十分攪拌混合する。次いで、これにより得られた混合物に酸化剤を滴下して重合を進行させてポリアニオンと導電性ポリマーとの複合体を得る。次いで、その複合体から、酸化剤、残留モノマー、副生成物を

除去、精製した後、適切な溶媒に溶解し、必要に応じてドーパントやバインダ樹脂を添加して導電性ポリマー塗料を得る。

[0053] 導電性ポリマー塗料の溶媒としては特に制限されず、例えば、水、Ｎ－メチル－２－ピロリドン、Ｎ，Ｎ－ジメチルホルムアミド、Ｎ，Ｎ－ジメチルアセトアミド、ジメチルスルホキシド、ヘキサメチレンホスホルトリアミド、アセトニトリル、ベンゾニトリル等の極性溶媒、クレゾール、フェノール、キシレノール等のフェノール類、メタノール、エタノール、プロパノール、ブタノール等のアルコール類、アセトン、メチルエチルケトン、メチルイソブチルケトン等のケトン類、酢酸メチル、酢酸エチル、酢酸プロピルなどのエステル類、ヘキサン、ベンゼン、トルエン、キシレン等の炭化水素類、ギ酸、酢酸等のカルボン酸、エチレンカーボネート、プロピレンカーボネート等のカーボネート化合物、ジオキサン、ジエチルエーテル等のエーテル化合物、エチレングリコールアルキルエーテル、プロピレングリコールアルキルエーテル、ポリエチレングリコールアルキルエーテル、ポリプロピレングリコールアルキルエーテル等の鎖状エーテル類、３－メチル－２－オキサゾリジノン等の複素環化合物、アセトニトリル、グルタロジニトリル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリル等のニトリル化合物等が挙げられる。これらの溶媒は、単独で用いてもよいし、２種類以上の混合物としてもよいし、他の有機溶媒との混合物としてもよい。

[0054] 本発明の透明導電ガラス基板は、後述するように、望ましくはフッ化水素酸によるエッチングによって表面を成型することから、この表面への濡れ性を向上させるために水に可溶な溶剤を５質量％以上含むことが好ましく、１０質量％以上含むことがより望ましい。ここで、水に可溶とは、２５℃の水１００ｇに対して１ｇ以上溶解するものである。

[0055] これは、前述した導電性ポリマーとポリアニオンとの複合体は、ポリアニオンが水溶性を示すことから水溶液であることが最も安定なこともあり、水に可溶な溶剤を選択することが望ましいものである。ただし、水以外の溶剤の割合が多くなりすぎると導電性ポリマーが溶液に分散できなくなって塗料

としての形態を保てなくなることから、水に可溶な溶剤は９９質量％以下が好ましく、９５質量％以下が望ましい。

[0056] さらに後述するように、導電性ポリマー塗料の乾燥、硬化を低温で行う必要性から溶媒の沸点は２００℃以下であることが好ましく、１８０℃以下であることが望ましい。しかしながら、スリット系のコーターなどの塗工時の作業性、レベリング性、ブラッシング防止などの観点からは、溶媒の沸点は５０℃以上が好ましく、７０℃以上がより好ましい。

[0057] （バインダ）

本発明の透明導電ガラス基板は液晶ディスプレイ等の電極等として用いられるため、液晶材料など種々の有機物が存在した状態で硬化させる必要がある。このため硬化温度が水や有機溶剤などの蒸散も含めて１２０℃以下の温度で硬化させる必要がある。このような架橋の例として赤外線、紫外線等の照射、加熱による硬化が有効である。紫外線照射による硬化の場合多官能アクリル基を有する化合物、増感剤、光開始剤を添加することによって硬化が達成できる。また熱硬化の場合には、バインダを添加しそれを硬化することによって導電性ポリマーを固定化することも可能であり、またポリアニオンを架橋させることも可能である。比較的短時間で１２０℃以下の温度で硬化させるためには架橋剤として多官能エポキシ化合物、多官能オキセタン化合物、多官能アジリジン化合物などを用い、更にはこれらとの反応性の高いポリマーカルボン酸や硬化触媒を用いることが推奨される。また、水溶性或いはエマルジョン化した多官能のカルボジイミドなども使用できる。

[0058] ［バインダ樹脂］

導電性ポリマー塗料は、塗膜の環境耐久性や耐傷性が高くなり、基材との密着性が向上することから、バインダ樹脂を含むことが好ましい。導電性ポリマー塗料がバインダ樹脂を含むことにより、導電性ポリマー塗料から形成された導電性ポリマー膜の鉛筆硬度（ＪＩＳ　Ｋ　５４００）をＨＢ以上にしやすい。すなわち、バインダ樹脂はハードコート成分としての機能を発揮する。

[0059] バインダ樹脂としては、導電性ポリマー塗料と相溶又は混合分散可能であれば熱硬化性樹脂であってもよいし、熱可塑性樹脂であってもよい。例えば、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエチレンナフタレート等のポリエステル；ポリイミド、ポリアミドイミド等のポリイミド；ポリアミド６、ポリアミド６，６、ポリアミド１２、ポリアミド１１等のポリアミド；ポリフッ化ビニリデン、ポリフッ化ビニル、ポリテトラフルオロエチレン、エチレンテトラフルオロエチレンコポリマー、ポリクロロトリフルオロエチレン等のフッ素樹脂；ポリビニルアルコール、ポリビニルエーテル、ポリビニルブチラール、ポリ酢酸ビニル、ポリ塩化ビニル等のビニル樹脂；エポキシ樹脂；オキセタン樹脂；アジリジン樹脂：オキサゾリン樹脂：キシレン樹脂；アラミド樹脂；ポリイミドシリコーン；ポリウレタン；ポリウレア；メラミン樹脂；フェノール樹脂；ポリエーテル；アクリル樹脂及びこれらの共重合体等が挙げられる。

[0060] これらバインダ樹脂は、有機溶剤に溶解されていてもよいし、スルホ基やカルボキシ基などの官能基が付与されて水溶液化されていてもよいし、乳化など水に分散されていてもよい。

[0061] また、バインダ樹脂には、必要に応じて、架橋剤、重合開始剤等の硬化剤、重合促進剤、溶媒、粘度調整剤等を加えて使用することができる。

[0062] バインダ樹脂の中でも、容易に混合できることから、ポリウレタン、ポリエステル、アクリル樹脂、ポリアミド、ポリイミド、エポキシ樹脂、オキセタン樹脂、アジリジン樹脂、メラミン樹脂、ポリイミドシリコーンのいずれか１種以上が好ましい。また、アクリル樹脂は、硬度が硬いとともに透明性に優れるため、ガラス基板のような用途には適している。

[0063] また、バインダ樹脂は、熱エネルギー及び／又は光エネルギーによって硬化する液状重合体を含むことが好ましい。

[0064] ここで、熱エネルギーにより硬化する液状重合体としては、反応型重合体及び自己架橋型重合体が挙げられる。

[0065] 反応型重合体は、置換基を有する単量体が重合した重合体であり、置換基

としては、ヒドロキシ基、カルボキシ基、酸無水物、オキセタン基、グリシジル基、アミノ基などが挙げられる。具体的な単量体としては、エチレングリコール、ジエチレングリコール、ジプロピレングリコール、グリセリン等の多官能アルコール、マロン酸、コハク酸、グルタミン酸、ピメリン酸、アスコルビン酸、フタル酸、アセチルサルチル酸、アジピン酸、イソフタル酸、安息香酸、ｍ－トルイル酸等のカルボン酸化合物、無水マレイン酸、無水フタル酸、ドデシル無水コハク酸、ジクロル無水マレイン酸、テトラクロル無水フタル酸、テトラヒドロ無水フタル酸、無水ピメリット酸等の酸無水物、３，３－ジメチルオキセタン、３，３－ジクロロメチルオキセタン、３－メチル－３－ヒドロキシメチルオキセタン、アジドメチルメチルオキセタン等のオキセタン化合物、ビスフェノールＡジグリシジルエーテル、ビスフェノールＦジグリシジルエーテル、フェノールノボラックポリグリシジルエーテル、Ｎ，Ｎ－ジグリシジル－ｐ－アミノフェノールグリシジルエーテル、テトラブロモビスフェノールＡジグリシジルエーテル、水添ビスフェノールＡジグリシジルエーテル（すなわち、２，２－ビス（４－グリシジルオキシシクロヘキシル）プロパン）、ネオペンチルグリコールジグリシジルエーテル、１，６－ヘキサンジオールジグリシジルエーテル、トリメチロールプロパンポリグリシジルエーテル、ヘキサヒドロフタル酸ジグリシジルエステル、プロピレングリコールジグリシジルエーテル、トリプロピレングリコールジグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル、脂肪酸変性エポキシ、ジエチレングリコールジグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、グリセリンポリグリシジルエーテル、ジグリセリンポリグリシジルエーテル、ポリグリセリンポリグリシジルエーテル、ソルビトール系ポリグリシジルエーテル、エチレンオキシドラウリルアルコールグリシジルエーテル、エチレンオキシドフェノールグリシジルエーテル、アジピン酸グリシジルエーテル等のグリシジルエーテル化合物、Ｎ，Ｎ－ジグリシジルアニリン、テトラグリシジルジアミノジフェニルメタン、Ｎ，Ｎ，Ｎ，Ｎ－テトラグリシジル－ｍ－キシリレンジアミン、トリ

グリシジルイソシアヌレート、Ｎ，Ｎ－ジグリシジル－５，５－ジアルキルヒダントイン等のグリシジルアミン化合物、ジエチレントリアミン、トリエチレンテトラミン、ジメチルアミノプロピルアミン、Ｎ－アミノエチルピペラジン、ベンジルジメチルアミン、トリス（ジメチルアミノメチル）フェノール、ＤＨＰ３０－トリ（２－エチルヘクソエート）、メタフェニレンジアミン、ジアミノジフェニルメタン、ジアミノジフェニルスルホン、ジシアンジアミド、三フッ化ホウ素、モノエチルアミン、メタンジアミン、キシレンジアミン、エチルメチルイミダゾール等のアミン化合物、１分子中に２個以上のオキシラン環を含む化合物のうち、ビスフェノールＡのエピクロロヒドリンによるグリシジル化合物、あるいはその類似物が挙げられる。

[0066] 反応型重合体においては、架橋剤や、触媒、後述するカチオン重合開始剤などを併用しても良い。架橋剤としては、例えば、メラミン樹脂、エポキシ樹脂、金属酸化物などが挙げられる。金属酸化物としては、塩基性金属化合物のＡｌ（ＯＨ）$_3$、Ａｌ（ＯＯＣ・ＣＨ$_3$）$_2$（ＯＯＣＨ）、Ａｌ（ＯＯＣ・ＣＨ$_3$）$_2$、ＺｒＯ（ＯＣＨ$_3$）、Ｍｇ（ＯＯＣ・ＣＨ$_3$）、Ｃａ（ＯＨ）$_2$、Ｂａ（ＯＨ）$_3$等を適宜使用できる。

[0067] 自己架橋型重合体は、加熱により官能基同士で自己架橋するものであり、例えば、グリシジル基とカルボキシ基を含むもの、あるいは、Ｎ－メチロールとカルボキシ基の両方を含むものなどが挙げられる。

[0068] 光エネルギーによって硬化する液状重合体としては、例えば、ポリエステル、エポキシ樹脂、オキセタン樹脂、ポリアクリル、ポリウレタン、ポリイミド、ポリアミド、ポリアミドイミド、ポリイミドシリコーン等のオリゴマー又はプレポリマーが挙げられる。

[0069] 光エネルギーによって硬化する液状重合体を構成する単量体単位としては、例えば、ビスフェノールＡ・エチレンオキサイド変性ジアクリレート、ジペンタエリスリトールヘキサ（ペンタ）アクリレート、ジペンタエリスリトールモノヒドロキシペンタアクリレート、ジプロピレングリコールジアクリレート、トリメチロールプロパントリアクリレート、グリセリンプロポキシ

トリアクリレート、４－ヒドロキシブチルアクリレート、１，６－ヘキサンジオールジアクリレート、２－ヒドロキシエチルアクリレート、２－ヒドロキシプロピルアクリレート、イソボルニルアクリレート、ポリエチレングリコールジアクリレート、ペンタエリスリトールトリアクリレート、テトラヒドロフルフリルアクリレート、トリメチロールプロパントリアクリレート、トリプロピレングリコールジアクリレート等のアクリレート類、テトラエチレングリコールジメタクリレート、アルキルメタクリレート、アリルメタクリレート、１，３－ブチレングリコールジメタクリレート、ｎ－ブチルメタクリレート、ベンジルメタクリレート、シクロヘキシルメタクリレート、ジエチレングリコールジメタクリレート、２－エチルヘキシルメタクリレート、グリシジルメタクリレート、１，６－ヘキサンジオールジメタクリレート、２－ヒドロキシエチルメタクリレート、イソボルニルメタクリレート、ラウリルメタクリレート、フェノキシエチルメタクリレート、ｔ－ブチルメタクリレート、テトラヒドロフルフリルメタクリレート、トリメチロールプロパントリメタクリレート等のメタクリレート類、アリルグリシジルエーテル、ブチルグリシジルエーテル、高級アルコールグリシジルエーデル、１，６－ヘキサンジオールグリシジルエーテル、フェニルグリシジルエーテル、ステアリルグリシジルエーテル等のグリシジルエーテル類、ダイアセトンアクリルアミド、Ｎ，Ｎ－ジメチルアクリルアミド、ジメチルアミノプロピルアクリルアミド、ジメチルアミノプロピルメタクリルアミド、メタクリルアミド、Ｎ－メチロールアクリルアミド、Ｎ，Ｎ－ジメチルアクリルアミド、アクリロイルモルホリン、Ｎ－ビニルホルムアミド、Ｎ－メチルアクリルアミド、Ｎ－イソプロピルアクリルアミド、Ｎ－ｔ－ブチルアクリルアミド、Ｎ－フェニルアクリルアミド、アクリロイルピペリジン、２－ヒドロキシエチルアクリルアミド等のアクリル（メタクリル）アミド類、２－クロロエチルビニルエーテル、シクロヘキシルビニルエーテル、エチルビニルエーテル、ヒドロキシブチルビニルエーテル、イソブチルビニルエーテル、トリエチレングリコールビニルエーテル等のビニルエーテル類、酪酸ビニル、モノクロ

ロ酢酸ビニル、ピバリン酸ビニル等のカルボン酸ビニルエステル類の単官能モノマー並びに多官能モノマーが挙げられる。

[0070] 光エネルギーによって硬化する液状重合体は、光重合開始剤によって硬化する。その光重合開始剤としては、アセトフェノン類、ベンゾフェノン類、ミヒラーベンゾイルベンゾエート、αーアミロキシムエステル、テトラメチルチウラムモノサルファイド、チオキサントン類などが挙げられる。さらに、光増感剤として、ｎーブチルアミン、トリエチルアミン、トリーｎーブチルホスフィン等を混合できる。

[0071] また、カチオン重合開始剤としては、アリールジアゾニウム塩類、ジアリールハロニウム塩類、トリフェニルスルホニウム塩類、シラノール／アルミニウムキレート、αースルホニルオキシケトン類等が挙げられる。

[0072] バインダ樹脂の含有量は導電性ポリマーとポリアニオンとの合計１００質量％に対して、１～１０００質量％であり、１０～４００質量％であることが好ましい。バインダ樹脂の含有量が１質量％未満であると、導電性ポリマー層の耐久性が不足することがあり、１０００質量％を超えると、導電性ポリマー層中の導電性ポリマーの含有量が少なくなり、充分な導電性が得られない。

[0073]（高導電化剤）

高導電化剤は、導電性高分子溶液から形成される導電性塗膜の導電性を向上させる成分である。

[0074] 具体的に、高導電化剤は、窒素含有芳香族性環式化合物、２個以上のヒドロキシ基を有する化合物、２個以上のカルボキシ基を有する化合物、１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物、アミド基を有する化合物、イミド基を有する化合物、ラクタム化合物、グリシジル基を有する化合物、シランカップリング剤、ＤＭＳＯ、水溶性有機溶媒からなる群より選ばれる少なくとも１種の化合物である。

[0075] ［窒素含有芳香族性環式化合物］

窒素含有芳香族性環式化合物としては、例えば、一つの窒素原子を含有す

るピリジン類及びその誘導体、二つの窒素原子を含有するイミダゾール類及びその誘導体、ピリミジン類及びその誘導体、ピラジン類及びその誘導体、三つの窒素原子を含有するトリアジン類及びその誘導体等が挙げられる。溶媒溶解性等の観点からは、ピリジン類及びその誘導体、イミダゾール類及びその誘導体、ピリミジン類及びその誘導体が好ましい。

[0076] ピリジン類及びその誘導体の具体的な例としては、ピリジン、２－メチルピリジン、３－メチルピリジン、４－メチルピリジン、４－エチルピリジン、Ｎ－ビニルピリジン、２，４－ジメチルピリジン、２，４，６－トリメチルピリジン、３－シアノ－５－メチルピリジン、２－ピリジンカルボン酸、６－メチル－２－ピリジンカルボン酸、４－ピリジンカルボキシアルデヒド、４－アミノピリジン、２，３－ジアミノピリジン、２，６－ジアミノピリジン、２，６－ジアミノ－４－メチルピリジン、４－ヒドロキシピリジン、４－ピリジンメタノール、２，６－ジヒドロキシピリジン、２，６－ピリジンジメタノール、６－ヒドロキシニコチン酸メチル、２－ヒドロキシ－５－ピリジンメタノール、６－ヒドロキシニコチン酸エチル、４－ピリジンメタノール、4－ピリジンエタノール、２－フェニルピリジン、３－メチルキノリン、３－エチルキノリン、キノリノール、２，３－シクロペンテノピリジン、２，３－シクロヘキサノピリジン、１，２－ジ（４－ピリジル）エタン、１，２－ジ（４－ピリジル）プロパン、２－ピリジンカルボキシアルデヒド、２－ピリジンカルボン酸、２－ピリジンカルボニトリル、２，３－ピリジンジカルボン酸、２，４－ピリジンジカルボン酸、２，５－ピリジンジカルボン酸、２，６－ピリジンジカルボン酸、３－ピリジンスルホン酸等が挙げられる。

[0077] イミダゾール類及びその誘導体の具体的な例としては、イミダゾール、２－メチルイミダゾール、２－プロピルイミダゾール、２－ウンデジルイミダゾール、２－フェニルイミダゾール、Ｎ－メチルイミダゾール、Ｎ－ビニルイミダゾール、Ｎ－アリルイミダゾール、１－（２－ヒドロキシエチル）イミダゾール（Ｎ－ヒドロキシエチルイミダゾール）、２－エチル－４－メチルイミダゾール、１，２－ジメチルイミダゾール、１－ベンジル－２－メチ

ルイミダゾール、１－ベンジル－２－フェニルイミダゾール、１－シアノエチル－２－メチルイミダゾール、１－シアノエチル－２－エチル－４－メチルイミダゾール、２－フェニル－４，５－ジヒドロキシメチルイミダゾール、１－アセチルイミダゾール、４，５－イミダゾールジカルボン酸、４，５－イミダゾールジカルボン酸ジメチル、ベンズイミダゾール、２－アミノベンズイミダゾール、２－アミノベンズイミダゾール－２－スルホン酸、２－アミノ－１－メチルベンズイミダゾール、２－ヒドロキシベンズイミダゾール、２－（２－ピリジル）ベンズイミダゾール等が挙げられる。

[0078] ピリミジン類及びその誘導体の具体的な例としては、２－アミノ－４－クロロ－６－メチルピリミジン、２－アミノ－６－クロロ－４－メトキシピリミジン、２－アミノ－４，６－ジクロロピリミジン、２－アミノ－４，６－ジヒドロキシピリミジン、２－アミノ－４，６－ジメチルピリミジン、２－アミノ－４，６－ジメトキシピリミジン、２－アミノピリミジン、２－アミノ－４－メチルピリミジン、４，６－ジヒドロキシピリミジン、２，４－ジヒドロキシピリミジン－５－カルボン酸、２，４，６－トリアミノピリミジン、２，４－ジメトキシピリミジン、２，４，５－トリヒドロキシピリミジン、２，４－ピリミジンジオール等が挙げられる。

[0079] ピラジン類及びその誘導体の具体的な例としては、ピラジン、２－メチルピラジン、２，５－ジメチルピラジン、ピラジンカルボン酸、２，３－ピラジンジカルボン酸、５－メチルピラジンカルボン酸、ピラジンアミド、５－メチルピラジンアミド、２－シアノピラジン、アミノピラジン、３－アミノピラジン－２－カルボン酸、２－エチル－３－メチルピラジン、２，３－ジメチルピラジン、２，３－ジエチルピラジン等が挙げられる。

[0080] トリアジン類及びその誘導体の具体的な例としては、１，３，５－トリアジン、２－アミノ－１，３，５－トリアジン、３－アミノ－１，２，４－トリアジン、２，４－ジアミノ－６－フェニル－１，３，５－トリアジン、２，４，６－トリアミノ－１，３，５－トリアジン、２，４，６－トリス（トリフルオロメチル）－１，３，５－トリアジン、２，４，６－トリ－２－ピ

リジン－１，３，５－トリアジン、３－（２－ピリジン）－５，６－ビス（４－フェニルスルホン酸）－１，２，４－トリアジン二ナトリウム、３－（２－ピリジン）－５，６－ジフェニル－１，２，４－トリアジン、３－（２－ピリジン）－５，６－ジフェニル－１，２，４－トリアジン－ρ，ρ’－ジスルホン酸二ナトリウム、２－ヒドロキシ－４，６－ジクロロ－１，３，５－トリアジン等が挙げられる。

[0081] 窒素含有芳香族性環式化合物の含有量は、ポリアニオンのアニオン基単位１モルに対して０．１～１００モルの範囲であることが好ましく、０．５～３０モルの範囲であることがより好ましく、導電性塗膜の物性及び導電性の観点からは、１～１０モルの範囲が特に好ましい。窒素含有芳香族性環式化合物の含有率が０．１モルより少なくなると、窒素含有芳香族性環式化合物とポリアニオン及び共役系導電性高分子との相互作用が弱くなる傾向にあり、導電性が不足することがある。また、窒素含有芳香族性環式化合物が１００モルを超えて含まれると共役系導電性高分子の含有量が少なくなり、やはり充分な導電性が得られにくい。

[0082] ［２個以上のヒドロキシ基を有する化合物］

２個以上のヒドロキシ基を有する化合物としては、例えば、プロピレングリコール、１，３－ブチレングリコール、１，４－ブチレングリコール、Ｄ－グルコース、Ｄ－グルシトール、イソプレングリコール、ジメチロールプロピオン酸、ブタンジオール、１，５－ペンタンジオール、１，６－ヘキサンジオール、１，９－ノナンジオール、ネオペンチルグリコール、トリメチロールエタン、トリメチロールプロパン、ペンタエリスリトール、ジペンタエリスリトール、チオジエタノール、グルコース、酒石酸、Ｄ－グルカル酸、グルタコン酸等の多価脂肪族アルコール類；セルロース、多糖、糖アルコール等の高分子アルコール；１，４－ジヒドロキシベンゼン、１，３－ジヒドロキシベンゼン、２，３－ジヒドロキシ－１－ペンタデシルベンゼン、２，４－ジヒドロキシアセトフェノン、２，５－ジヒドロキシアセトフェノン、２，４－ジヒドロキシベンゾフェノン、２，６－ジヒドロキシベンゾフェ

ノン、３，４－ジヒドロキシベンゾフェノン、３，５－ジヒドロキシベンゾフェノン、２，４’－ジヒドロキシジフェニルスルフォン、２，２’，５，５’－テトラヒドロキシジフェニルスルフォン、３，３’，５，５’－テトラメチル－４，４’－ジヒドロキシジフェニルスルフォン、ヒドロキシキノンカルボン酸及びその塩類、２，３－ジヒドロキシ安息香酸、２，４－ジヒドロキシ安息香酸、２，５－ジヒドロキシ安息香酸、２，６－ジヒドロキシ安息香酸、３，５－ジヒドロキシ安息香酸、１，４－ヒドロキノンスルホン酸及びその塩類、４，５－ヒドロキシベンゼン－１，３－ジスルホン酸及びその塩類、１，５－ジヒドロキシナフタレン、１，６－ジヒドロキシナフタレン、２，６－ジヒドロキシナフタレン、２，７－ジヒドロキシナフタレン、２，３－ジヒドロキシナフタレン、１，５－ジヒドロキシナフタレン－２，６－ジカルボン酸、１，６－ジヒドロキシナフタレン－２，５－ジカルボン酸、１，５－ジヒドロキシナフトエ酸、１，４－ジヒドロキシ－２－ナフトエ酸フェニルエステル、４，５－ジヒドロキシナフタレン－２，７－ジスルホン酸及びその塩類、１，８－ジヒドロキシ－３，６－ナフタレンジスルホン酸及びその塩類、６，７－ジヒドロキシ－２－ナフタレンスルホン酸及びその塩類、１，２，３－トリヒドロキシベンゼン（ピロガロール）、１，２，４－トリヒドロキシベンゼン、５－メチル－１，２，３－トリヒドロキシベンゼン、５－エチル－１，２，３－トリヒドロキシベンゼン、５－プロピル－１，２，３－トリヒドロキシベンゼン、トリヒドロキシ安息香酸、トリヒドロキシアセトフェノン、トリヒドロキシベンゾフェノン、トリヒドロキシベンゾアルデヒド、トリヒドロキシアントラキノン、２，４，６－トリヒドロキシベンゼン、テトラヒドロキシ－ｐ－ベンゾキノン、テトラヒドロキシアントラキノン、ガーリック酸メチル（没食子酸メチル）、ガーリック酸エチル（没食子酸エチル）等の芳香族化合物、ヒドロキノンスルホン酸カリウム等が挙げられる。

[0083] ２個以上のヒドロキシ基を有する化合物の含有量は、ポリアニオンのアニオン基単位１モルに対して０．０５～５０モルの範囲であることが好ましく

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、０．３～１０モルの範囲であることがより好ましい。２個以上のヒドロキシ基を有する化合物の含有量が、ポリアニオンのアニオン基単位１モルに対して０．０５モルより少なくなると、導電性及び耐熱性が不足することがある。また、２個以上のヒドロキシ基を有する化合物の含有量が、ポリアニオンのアニオン基単位１モルに対して５０モルより多くなると、導電性塗膜中のπ共役系導電性高分子の含有量が少なくなり、やはり充分な導電性が得られにくい。

[0084] ［２個以上のカルボキシ基を有する化合物］

２個以上のカルボキシ基を有する化合物としては、マレイン酸、フマル酸、イタコン酸、シトラコン酸、マロン酸、１，４－ブタンジカルボン酸、コハク酸、酒石酸、アジピン酸、Ｄ－グルカル酸、グルタコン酸、クエン酸等の脂肪族カルボン酸類化合物；フタル酸、テレフタル酸、イソフタル酸、テトラヒドロ無水フタル酸、５－スルホイソフタル酸、５－ヒドロキシイソフタル酸、メチルテトラヒドロ無水フタル酸、４，４’－オキシジフタル酸、ビフェニルテトラカルボン酸二無水物、ベンゾフェノンテトラカルボン酸二無水物、ナフタレンジカルボン酸、トリメリット酸、ピロメリット酸等の、芳香族性環に少なくとも一つ以上のカルボキシ基が結合している芳香族カルボン酸類化合物；ジグリコール酸、オキシ二酪酸、チオ二酢酸（チオジ酢酸）、チオ二酪酸、イミノ二酢酸、イミノ酪酸等が挙げられる。

[0085] ２個以上のカルボキシ基を有する化合物は、ポリアニオンのアニオン基単位１モルに対して０．１～３０モルの範囲であることが好ましく、０．３～１０モルの範囲であることがより好ましい。２個以上のカルボキシ基を有する化合物の含有量が、ポリアニオンのアニオン基単位１モルに対して０．１モルより少なくなると、導電性及び耐熱性が不足することがある。また２個以上のカルボキシ基を有する化合物の含有量が、ポリアニオンのアニオン基単位１モルに対して３０モルより多くなると、導電性塗膜中のπ共役系導電性高分子の含有量が少なくなり、やはり充分な導電性が得られにくく、導電性塗膜の物性が変化することがある。

[0086] ［１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物］

１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物としては、酒石酸、グリセリン酸、ジメチロールブタン酸、ジメチロールプロパン酸、Ｄ－グルカル酸、グルタコン酸等が挙げられる。

[0087] １個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物の含有量は、ポリアニオンとπ共役系導電性高分子の合計１００質量部に対して１～５０００質量部であることが好ましく、５０～５００質量部であることがより好ましい。１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物の含有量が１質量部より少なくなると、導電性及び耐熱性が不足することがある。また、１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物の含有量が５０００質量部より多くなると、導電性塗膜中のπ共役系導電性高分子の含有量が少なくなり、やはり充分な導電性が得ることが難しい。

[0088] ［アミド化合物］

アミド基を有する化合物は、－ＣＯ－ＮＨ－（ＣＯの部分は二重結合）で表されるアミド結合を分子中に有する単分子化合物である。すなわち、アミド化合物としては、例えば、上記結合の両末端に官能基を有する化合物、上記結合の一方の末端に環状化合物が結合された化合物、上記両末端の官能基が水素である尿素及び尿素誘導体などが挙げられる。

[0089] アミド化合物の具体例としては、アセトアミド、マロンアミド、スクシンアミド、マレアミド、フマルアミド、ベンズアミド、ナフトアミド、フタルアミド、イソフタルアミド、テレフタルアミド、ニコチンアミド、イソニコチンアミド、２－フルアミド、ホルムアミド、Ｎ－メチルホルムアミド、プロピオンアミド、プロピオルアミド、ブチルアミド、イソブチルアミド、メタクリルアミド、パルミトアミド、ステアリルアミド、オレアミド、オキサミド、グルタルアミド、アジプアミド、シンナムアミド、グリコールアミド、ラクトアミド、グリセルアミド、タルタルアミド、シトルアミド、グリオキシルアミド、ピルボアミド、アセトアセトアミド、ジメチルアセトアミド

、ベンジルアミド、アントラニルアミド、エチレンジアミンテトラアセトアミド、ジアセトアミド、トリアセトアミド、ジベンズアミド、トリベンズアミド、ローダニン、尿素、１－アセチル－２－チオ尿素、ビウレット、ブチル尿素、ジブチル尿素、１，３－ジメチル尿素、１，３－ジエチル尿素及びこれらの誘導体等が挙げられる。

[0090] また、アミド化合物として、アクリルアミドを使用することもできる。アクリルアミドとしては、Ｎ－メチルアクリルアミド、Ｎ－メチルメタクリルアミド、Ｎ－エチルアクリルアミド、Ｎ－エチルメタクリルアミド、Ｎ，Ｎ－ジメチルアクリルアミド、Ｎ，Ｎ－ジメチルメタクリルアミド、Ｎ，Ｎ－ジエチルアクリルアミド、Ｎ，Ｎ－ジエチルメタクリルアミド、２－ヒドロキシエチルアクリルアミド、２－ヒドロキシエチルメタクリルアミド、Ｎ－メチロールアクリルアミド、Ｎ－メチロールメタクリルアミドなどが挙げられる。

[0091] アミド化合物の分子量は４６～１００００であることが好ましく、４６～５０００であることがより好ましく、４６～１０００であることが特に好ましい。

[0092] アミド化合物の含有量は、ポリアニオンとπ共役系導電性高分子の合計１００質量部に対して１～５０００質量部であることが好ましく、５０～５００質量部であることがより好ましい。アミド化合物の含有量が１質量部より少なくなると、導電性及び耐熱性が不足することがある。また、アミド化合物の含有量が５０００質量部より多くなると、導電性塗膜中のπ共役系導電性高分子の含有量が少なくなり、やはり充分な導電性が得ることが難しい。

[0093] ［イミド化合物］

アミド化合物としては、導電性がより高くなることから、イミド結合を有する単分子化合物（以下、イミド化合物という。）が好ましい。イミド化合物としては、その骨格より、フタルイミド及びフタルイミド誘導体、スクシンイミド及びスクシンイミド誘導体、ベンズイミド及びベンズイミド誘導体、マレイミド及びマレイミド誘導体、ナフタルイミド及びナフタルイミド誘

導体などが挙げられる。

[0094] また、イミド化合物は両末端の官能基の種類によって、脂肪族イミド、芳香族イミド等に分類されるが、溶解性の観点からは、脂肪族イミドが好ましい。

[0095] さらに、脂肪族イミド化合物は、分子内の炭素間に不飽和結合を有する飽和脂肪族イミド化合物と、分子内の炭素間に不飽和結合を有する不飽和脂肪族イミド化合物とに分類される。

[0096] 飽和脂肪族イミド化合物は、R^1－ＣＯ－ＮＨ－ＣＯ－R^2で表される化合物であり、R^1，R^2の両方が飽和炭化水素である化合物である。具体的には、シクロヘキサン－１，２－ジカルボキシイミド、アラントイン、ヒダントイン、バルビツル酸、アロキサン、グルタルイミド、スクシンイミド、５－ブチルヒダントイン酸、５，５－ジメチルヒダントイン、１－メチルヒダントイン、１，５，５－トリメチルヒダントイン、５－ヒダントイン酢酸、Ｎ－ヒドロキシ－５－ノルボルネン－２，３－ジカルボキシイミド、セミカルバジド、α，α－ジメチル－６－メチルスクシンイミド、ビス［２－（スクシンイミドオキシカルボニルオキシ）エチル］スルホン、α－メチル－α－プロピルスクシンイミド、シクロヘキシルイミドなどが挙げられる。

[0097] 不飽和脂肪族イミド化合物は、R^1－ＣＯ－ＮＨ－ＣＯ－R^2で表される化合物であり、R^1，R^2の一方又は両方が１つ以上の不飽和結合である化合物である。具体例は、１，３－ジプロピレン尿素、マレイミド、Ｎ－メチルマレイミド、Ｎ－エチルマレイミド、Ｎ－ヒドロキシマレイミド、１，４－ビスマレイミドブタン、１，６－ビスマレイミドヘキサン、１，８－ビスマレイミドオクタン、Ｎ－カルボキシヘプチルマレイミドなどが挙げられる。

[0098] イミド化合物の分子量は６０～５０００であることが好ましく、７０～１０００であることがより好ましく、８０～５００であることが特に好ましい。

[0099] イミド化合物の含有量は、π共役系導電性高分子とポリアニオンの合計１００質量部に対して１０～１００００質量部であることが好ましく、５０～

５０００質量部であることがより好ましい。アミド化合物及びイミド化合物の添加量が前記下限値未満であると、アミド化合物及びイミド化合物添加による効果が低くなるため好ましくない。また、前記上限値を超えると、π共役系導電性高分子濃度の低下に起因する導電性の低下が起こるため好ましくない。

[0100] ［ラクタム化合物］

ラクタム化合物とは、アミノカルボン酸の分子内環状アミドであり、環の一部がーＣＯーＮＲー（Ｒは水素又は任意の置換基）である化合物である。ただし、環の一個以上の炭素原子が不飽和やヘテロ原子に置き換わっていてもよい。

ラクタム化合物としては、例えば、ペンタノー４ーラクタム、４ーペンタンラクタムー５ーメチルー２ーピロリドン、５ーメチルー２ーピロリジノン、ヘキサノー６ーラクタム、６ーヘキサンラクタム等が挙げられる。

[0101] ラクタム化合物の含有量は、π共役系導電性高分子とポリアニオンの合計１００質量部に対して１０～１００００質量部であることが好ましく、５０～５０００質量部であることがより好ましい。ラクタム化合物の添加量が前記下限値未満であると、ラクタム化合物添加による効果が低くなるため好ましくない。また、前記上限値を超えると、π共役系導電性高分子濃度の低下に起因する導電性の低下が起こるため好ましくない。

[0102] ［グリシジル基を有する化合物］

グリシジル基を有する化合物としては、例えば、エチルグリシジルエーテル、ブチルグリシジルエーテル、ｔーブチルグリシジルエーテル、アリルグリシジルエーテル、ベンジルグリシジルエーテル、グリシジルフェニルエーテル、ビスフェノールＡ、ジグリシジルエーテル、アクリル酸グリシジルエーテル、メタクリル酸グリシジルエーテル等のグリシジル化合物などが挙げられる。

[0103] グリシジル基を有する化合物の含有量は、π共役系導電性高分子とポリアニオンの合計１００質量部に対して１０～１００００質量部であることが好

ましく、５０～５０００質量部であることがより好ましい。グリシジル基を有する化合物の添加量が前記下限値未満であると、グリシジル基を有する化合物添加による効果が低くなるため好ましくない。また、前記上限値を超えると、π共役系導電性高分子濃度の低下に起因する導電性の低下が起こるため好ましくない。

[0104] ［シランカップリング剤］

シランカップリング剤の具体例としては、ビニルトリクロルシラン、ビニルトリメトキシシラン、ビニルトリエトキシシラン、２－（３，４－エポキシシクロヘキシル）エチルトリメトキシシラン、３－グリシドキシプロピルトリメトキシシラン、３－グリシドキシプロピルメチルジエトキシシラン、３－グリシドキシプロピルトリエトキシシラン、ｐ－スチリルトリメトキシシラン、３－メタクリロキシプロピルメチルジメトキシシラン、３－メタクリロキシプロピルトリメトキシシラン、３－メタクリロキシプロピルメチルジエトキシシラン、３－メタクリロキシプロピルトリエトキシシラン、３－アクリロキシプロピルトリメトキシシラン、Ｎ－２－（アミノエチル）－３－アミノプロピルメチルジメトキシシラン、Ｎ－２－（アミノエチル）－３－アミノプロピルトリエトキシシラン、Ｎ－
２－（アミノエチル）－３－アミノプロピルトリメトキシシラン、３－アミノプロピルトリメトキシシラン、３－アミノプロピルトリエトキシシラン、３－トリエトキシシリル－Ｎ－（１，３－ジメチル－ブチリデン）プロピルアミン、Ｎ－フェニル－３－アミノプロピルトリメトキシシラン、Ｎ－（ビニルベンジル）－２－アミノエチル－３－アミノプロピルトリメトキシシランの塩酸塩、３－ウレイドプロピルトリエトキシシラン、３－クロロプロピルトリメトキシシラン、３－メルカプトプロピルメチルジメトキシシラン、３－メルカプトプロピルトリメトキシシラン、ビス（トリエトキシシリルプロピル）テトラスルフィド、３－イソシアネートプロピルトリエトキシシランなどが挙げられる。

[0105] シランカップリング剤の含有量は、必要に応じて任意量を添加することが

でき、特に限定しない。π共役系導電性高分子とポリアニオンの合計１００質量部に対して１０～１００００質量部であることが好ましい。

実施例

[0106] 以下、本発明に係る実施例１～４と比較例１～３を、表１を参照して説明する。

[0107] （材料の調製）

［１］ポリスチレンスルホン酸の調製

１０００ｍｌのイオン交換水に２０６ｇのスチレンスルホン酸ナトリウムを溶解し、８０℃で攪拌しながら、予め１０ｍｌの水に溶解した１．１４ｇの過硫酸アンモニウム酸化剤溶液を２０分間滴下し、この溶液を２時間攪拌した。これにより得られたスチレンスルホン酸ナトリウム含有溶液に１０質量％に希釈した硫

酸を１０００ｍｌと１００００ｍｌのイオン交換水を添加し、限外ろ過法を用いてポリスチレンスルホン酸含有溶液の約１００００ｍｌ溶液を除去し、残液に１００００ｍｌのイオン交換水を加え、限外ろ過法を用いて約１００００ｍｌ溶液を除去した。上記の限外ろ過操作を３回繰り返した。さらに、得られたろ液に約１００００ｍｌのイオン交換水を添加し、限外ろ過法を用いて約１００００ｍｌ溶液を除去した。この限外ろ過操作を３回繰り返した。限外ろ過条件は下記の通りとした。

限外ろ過膜の分画分子量：３００００

クロスフロー式

供給液流量：３０００ｍｌ／分

膜分圧：０．１２Ｐａ

得られた溶液中の水を減圧除去して、無色の固形状のポリスチレンスルホン酸を得た。

[0108] ［２］ポリスチレンスルホン酸ドープポリ（３，４－エチレンジオキシチオフェン）水溶液の調製

１４．２ｇの３，４－エチレンジオキシチオフェンと、３６．７ｇの［１

］で得たポリスチレンスルホン酸を２０００ｍｌのイオン交換水に溶かした溶液とを２０℃で混合した。これにより得られた混合溶液を２０℃に保ち、掻き混ぜながら、２００ｍｌのイオン交換水に溶かした２９．６４ｇの過硫酸アンモニウムと８．０ｇの硫酸第二鉄の酸化触媒溶液とをゆっくり添加し、３時間攪拌して反応させた。得られた反応液に２０００ｍｌのイオン交換水を添加し、限外ろ過法を用いて約２０００ｍｌ溶液を除去した。この操作を３回繰り返した。そして、上記ろ過処理が行われた処理液に２００ｍｌの１０質量％に希釈した硫酸と２０００ｍｌのイオン交換水を加え、限外ろ過法を用いて約２０００ｍｌの処理液を除去し、これに２０００ｍｌのイオン交換水を加え、限外ろ過法を用いて約２０００ｍｌの液を除去した。この操作を３回繰り返した。さらに、得られた処理液に２０００ｍｌのイオン交換水を加え、限外ろ過法を用いて約２０００ｍｌの処理液を除去した。この操作を５回繰り返し、約１．５質量％の青色のポリスチレンスルホン酸ドープポリ（３，４－エチレンジオキシチオフェン）（ＰＥＤＯＴ－ＰＳＳ）水溶液を得た。限外ろ過条件は［１］と同様である。

[0109] ［３］ガラス基板の調製

フッ酸・塩酸・硝酸の混合液を用いてノニオンガラスをバブリングしながらケミカルエッチング（液温３８～４２℃）することによりにより、ガラス基板を作製した。このガラス基板の厚みは０．４ｍｍ、表面の水接触角は６．２度、算術平均粗さＲａは０．０００８μｍであった。

[0110] ［４］ガラス基板の調製

ブロアーを用いてノニオンガラスをバブリングしながらケミカルエッチング（液温３８～４２℃）することによりにより、ガラス基板を作製した。このガラス基板の厚みは０．４ｍｍ、表面の水接触角は６．２度、算術平均粗さＲａは０．１９５μｍであった。

[0111] ［５］ガラス基板の調製

ブロアーを用いてノニオンガラスをバブリングしながらケミカルエッチング（液温３８～４２℃）することによりにより、ガラス基板を作製した。こ

のガラス基板の厚みは２ｍｍ、表面の水接触角は６．２度、算術平均粗さＲａは０．０００８μｍであった。

[0112] （測定と評価）

（算術平均粗さＲａ）

ＪＩＳ　Ｂ　０６０１－２００１に準じて測定した。

[0113] （表面抵抗値）

三菱化学社製ロレスタＭＣＰ－Ｔ６００を用い、ＪＩＳ　Ｋ　７１９４に準じて測定した。

[0114] （光透過率）

日本電色工業社製ヘイズメータ測定器（ＮＤＨ５０００）を用い、ＪＩＳＫ７１３６に準じて光透過率を測定した。

[0115] （鉛筆硬度）

ＪＩＳ　Ｓ　６００６に規定された試験用鉛筆を用いて、ＪＩＳ　Ｋ　５６００に従い、７５０ｇの荷重の際に傷が認められない硬度を測定した。

[0116] （可撓性）

透明導電ガラス基板を半径（Ｒ）２５ｍｍの筒に１８０度接するように巻きつける⇔戻す操作を５回行い、その前後の表面抵抗値の変化を測定した。

[0117] （実施例１）

［２］で得たＰＥＤＯＴ－ＰＳＳ水溶液６００ｇに、ガーリック酸メチル３．６ｇ、イルガキュア１２７（チバ・スペシャルティ・ケミカルズ社製）０．９ｇ、ジメチルスルホキシド２０ｇ、ヒドロキシアクリレート２．５ｇ、ペンタエリスリトールトリアクリレート７．２ｇ、エタノール３００ｇを混合し、撹拌して、導電性高分子溶液Ａを得た。

[0118] 導電性高分子溶液Ａを［３］で得たガラス基板の１面に、インネクスト製型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１５０μｍ、塗付速度２０ｍｍ／ｓｅｃ、ワークディスタンス１００μｍ、吐出流量0.11ｍｌにより塗布し、１００℃、２分間、赤外線照射により乾燥した後、紫外線（高圧水銀灯１２０Ｗ、５００ｍＪ／ｃｍ^2、１７８ｍ

W／ｃｍ²）照射し、硬化させて、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを以下の方法により測定した。

[0119] （実施例２）

［２］で得たＰＥＤＯＴ－ＰＳＳ水溶液６００ｇに、ガーリック酸メチル３．６ｇ、イルガキュア１２７（チバ・スペシャルティ・ケミカルズ社製）０．９ｇ、ジメチルスルホキシド２０ｇ、ジエチレングリコールジグリシジルエーテル９．２ｇ、２－メチルイミダゾール０．２ｇ、エタノール２５０ｇ、エチレングリコール５０gを混合し、撹拌して、導電性高分子溶液Ｂを得た。

導電性高分子溶液Ｂを［３］で得たガラス基板の１面に、インネクスト製型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１５０μｍ、塗付速度４０ｍｍ／ｓｅｃ、ワークディスタンス１００μｍ、吐出流量０．３ｍｌにより塗布し、１２０℃、２分間、赤外線照射により乾燥して硬化させて、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0120] （実施例３）

ＰＥＤＯＴ－ＰＳＳ水溶液（クレビオス　ＰＨ１０００：スタルク社製）６００ｇに、ガーリック酸メチル３．６ｇ、イルガキュア１２７（チバ・スペシャルティ・ケミカルズ社製）０．９ｇ、ジメチルスルホキシド２０ｇ、ジエチレングリコールジグリシジルエーテル９．２ｇ、２－メチルイミダゾール０．２ｇ、ガーリック酸０．５ｇ、エタノール２５０ｇ、エチレングリコール５０gを混合し、撹拌して、導電性高分子溶液Ｃを得た。

導電性高分子溶液Ｃを［３］で得たガラス基板の１面に、インネクスト製型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１３０μｍ、塗付速度４０ｍｍ／ｓｅｃ、ワークディスタンス　１００μｍ、吐出流量０．２１ｍｌにより塗布し、１２０度、２分間、赤外線照射により乾燥して硬化させて、導電性塗膜を形成させた。導電性塗膜の表面

抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0121] （実施例４）

導電性高分子溶液Ｃを［４］で得たガラス基板の１面に、インネクスト製型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１３０μｍ、塗付速度６０ｍｍ／ｓｅｃ、ワークディスタンス８０μｍ、吐出流量０．６ｍｌにより塗布し、１２０℃、２分間、赤外線照射により乾燥して硬化させて、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0122] （実施例５）

［２］で得たＰＥＤＯＴ－ＰＳＳ水溶液５００ｇに、２－メチルイミダゾール２ｇ、水分散性ポリエステル樹脂（バイロナールＭＤ１４８０：固形分２５質量％）１５０ｇ、ガーリック酸３．６ｇ、ジメチルスルホキシド２０ｇ、メタノール１５００ｇを混合し、撹拌して、導電性高分子溶液Ｄを得た。この導電性高分子溶液Ｄを［３］で得たガラス基板の１面に、インネクスト製　型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１５０μｍ、塗付速度　４０ｍｍ／ｓｅｃ、ワークディスタンス　１００μｍ、吐出流量　０．３ｍｌにより塗布し、１２０℃、２分間、赤外線照射により乾燥して、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0123] （比較例１）

［３］で得たガラス基板の１面に、スパッタリングによりＩＴＯ膜を形成し、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0124] （比較例２）

［４］で得たガラス基板の１面に、スパッタリングによりＩＴＯ膜を形成し、導電性塗膜を形成させた。導電性塗膜の表面抵抗と光透過率、鉛筆硬度、透明導電ガラス基板の可撓性とを測定した。

[0125] （比較例３）

導電性高分子溶液Ｃを［５］で得たガラス基板の１面に、インネクスト製型番ＩＳ－７９００ＩＬ－ＮＳＣのスリットコーターを用い、ノズルギャップ　１３０μｍ、塗付速度６０ｍｍ／ｓｅｃ、ワークディスタンス８０μｍ、吐出流量０．６ｍｌにより塗布したところ、導電性塗膜の表面抵抗、光透過率及び鉛筆硬度は測定不能で、透明導電ガラス基板の可撓性測定では、試料が破損した。

[0126] 表１は、実施例１～４と比較例１～３の結果を比較したものである。

[0127] [表1]

	表面抵抗（Ω／□）	光線透過率（%）	鉛筆硬度	可撓性
実施例１	300～600	88～89	2H	変化率　1.2倍
実施例２	500～1000	88～89	3H	変化率　1.2倍
実施例３	400～800	88～90	3H	変化率　1.1倍
実施例４	1000～2000	88～90	2H	変化率　1.3倍
実施例５	1.2×10^{7}～1.8×10^{9}	89～91	H	変化率　1.2倍
比較例１	400～1000	85～88	3H	変化率　1.1倍
比較例２	測定不能	測定不能	測定不能	破損
比較例３	測定不能	測定不能	測定不能	破損

[0128] 以上、実施形態を用いて本発明を説明したが、本発明の技術的範囲は上記実施形態に記載の範囲には限定されないことは言うまでもない。上記実施形態に、多様な変更または改良を加えることが可能であることが当業者に明らかである。またその様な変更または改良を加えた形態も本発明の技術的範囲に含まれ得ることが、特許請求の範囲の記載から明らかである。

産業上の利用可能性

[0129] 本発明の透明導電ガラス基板は、ＶＡ方式液晶、ＴＮ方式液晶、ＩＰＳ方式液晶などのガラス基板材料として用いられ、液晶駆動電極やＩＰＳの視野角阻害を起こす液晶表面帯電の防止として使用される。これらに用いられる

透明導電ガラス基板は生産歩留まりの理由から、先に液晶を封入した後に導電性ポリマーを塗布することがあり、この場合、液晶材料は熱に弱い有機材料であるため、液晶材料の熱変性防止のために上記導電性ポリマー層の乾燥、硬化などの温度は２００℃以下であることが好ましく、１６０℃以下であることが望ましい。なお、従来、ＩＴＯ成膜時は、高真空環境下で実施されることから、ＩＴＯ成膜前に液晶が封入されていると、液晶が減圧膨張し、ガラスが破壊される。導電性ポリマーによる透明導電膜は、高真空等の減圧された環境は必要なく、常圧で施工できることから、真空中の破壊がなくなるといった利点も有する。

請求の範囲

［請求項1］ ガラス基板上の少なくとも一面に導電性ポリマー層を有し、表面抵抗が１．８ＧΩ／□以下、全光線透過率が８５％以上、表面鉛筆硬度Ｈ以上、Ｒ
２５ｍｍの折り曲げで破損しないことを特徴とする透明導電ガラス基板。

［請求項2］ 前記導電性ポリマー層を形成する導電性ポリマー塗料が、導電性ポリマー及びポリアニオンを含み、さらにバインダ、硬化剤、高導電化剤、界面活性剤、触媒及び接着性向上剤を含む群から選択される１つ又は複数を含むことを特徴とする請求項１に記載の透明導電ガラス基板。

［請求項3］ 前記導電性ポリマーは、主鎖がπ共役系で構成されている有機高分子である、ポリピロール類、ポリチオフェン類、ポリアセチレン類、ポリフェニレン類、ポリフェニレンビニレン類、ポリアニリン類、ポリアセン類、ポリチオフェンビニレン類、及びそれらの共重合体を含む群から選択される１つ又は複数に属する１つ又は複数のポリマーからなることを特徴とする請求項２に記載の透明導電ガラス基板。

［請求項4］ 前記導電性ポリマーは、少なくともポリマーアニオンとチオフェンまたはチオフェン誘導体のポリマーとを含むことを特徴とする請求項２又は３に記載の透明導電ガラス基板。

［請求項5］ 前記ポリマーアニオンはポリスチレンスルホン酸であり、前記チオフェンまたはチオフェン誘導体のポリマーはポリ－３，４－エチレンジオキシチオフェンであることを特徴とする請求項４に記載の透明導電ガラス基板。

［請求項6］ 前記ポリアニオンは、一置換硫酸エステル基、一置換リン酸エステル基、リン酸基、カルボキシ基及びスルホ基を含む群から選択される１つ又は複数のアニオン基を有する１つ又は複数のポリマーを含むことを特徴とする請求項２に記載の透明導電ガラス基板。

［請求項7］　前記バインダはバインダ樹脂であり、前記バインダ樹脂が、１つ又は複数の、前記導電性ポリマー塗料と相溶又は混合分散可能な熱硬化性樹脂及び／又は熱可塑性樹脂であることを特徴とする請求項２に記載の透明導電ガラス基板。

［請求項8］　前記高導電化剤は、窒素含有芳香族性環式化合物、２個以上のヒドロキシ基を有する化合物、２個以上のカルボキシ基を有する化合物、１個以上のヒドロキシ基及び１個以上のカルボキシ基を有する化合物、アミド基を有する化合物、イミド基を有する化合物、ラクタム化合物、グリシジル基を有する化合物、シランカップリング剤、ＤＭＳＯ及び水溶性有機溶媒からなる群より選択される１つ又は複数の化合物であることを特徴とする請求項２に記載の透明導電ガラス基板。

［請求項9］　前記導電性ポリマー塗料は、沸点が５０～２００℃の範囲であり且つ水に可溶の溶剤を５～９５質量％含むことを特徴とする特許請求項２～８のいずれか１項に記載の透明導電ガラス基板。

［請求項10］　前記導電性ポリマー層は、前記導電性ポリマー塗料の塗布に続き、乾燥及び加熱並びに／又は赤外線もしくは紫外線の照射の工程を経て作製されたものであることを特徴とする請求項１～９のいずれか１項に記載の透明導電ガラス基板。

［請求項11］　前記導電性ポリマー塗料の塗布は、スクリーン印刷法、グラビア印刷法、フレキソ印刷法、オフセット印刷法、インクジェット印刷法、スピンコート法、スリットコーター法を含むダイコート法、カーテンコート法及びキャップコート法を含む群から選択されるいずれかの方法によって行うことを特徴とする請求項１０に記載の透明導電ガラス基板。

［請求項12］　前記ガラス基板の厚みが０．０３～０．７ｍｍの範囲にあり、ガラス表面の水に対する接触角が５～４０度の範囲にあることを特徴とする請求項１に記載の透明導電ガラス基板。

［請求項13］　前記ガラス基板上の少なくとも前記導電性ポリマー層を有する面が

フッ化水素酸含有混合液によるエッチングによって成形された部位を含むものであることを特徴とする請求項１又は１２に記載の透明導電ガラス基板。

［請求項14］ 前記導電性ポリマー層は、加熱及び/又は赤外線もしくは紫外線の照射によって硬化されたものであることを特徴とする請求項１～１３のいずれか１項に記載の透明導電ガラス基板。

［請求項15］ 前記導電性ポリマー層は１６０℃以下の温度で硬化されてなることを特徴とする請求項１～１４のいずれか１項に記載の透明導電ガラス基板。

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/074797

A. CLASSIFICATION OF SUBJECT MATTER
H01B5/14(2006.01)i, *G02F1/1333*(2006.01)i, *H01B13/00*(2006.01)i

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)
H01B5/14, G02F1/1333, H01B13/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2010-159365 A (Shin-Etsu Polymer Co., Ltd.), 22 July 2010 (22.07.2010), claims; paragraphs [0054], [0082] to [0083], [0087], [0103], [0115] to [0123] (Family: none)	1-11,14-15 12-13
Y	JP 2001-113635 A (Oji Paper Co., Ltd.), 24 April 2001 (24.04.2001), claims (Family: none)	1-11,14-15
Y	JP 2006-28439 A (Shin-Etsu Polymer Co., Ltd.), 02 February 2006 (02.02.2006), claims; paragraphs [0027], [0045] (Family: none)	1-11,14-15

☐ 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 application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"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
18 November, 2011 (18.11.11)	29 November, 2011 (29.11.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

国際調査報告	国際出願番号　ＰＣＴ／ＪＰ２０１１／０７４７９７

Ａ．　発明の属する分野の分類（国際特許分類（ＩＰＣ））

Int.Cl.　H01B5/14(2006.01)i, G02F1/1333(2006.01)i, H01B13/00(2006.01)i

Ｂ．　調査を行った分野

調査を行った最小限資料（国際特許分類（ＩＰＣ））

Int.Cl.　H01B5/14, G02F1/1333, H01B13/00

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	１９２２－１９９６年
日本国公開実用新案公報	１９７１－２０１１年
日本国実用新案登録公報	１９９６－２０１１年
日本国登録実用新案公報	１９９４－２０１１年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

Ｃ．　関連すると認められる文献

引用文献のカテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求項の番号
Y A	JP 2010-159365 A（信越ポリマー株式会社）2010.07.22,　【特許請求の範囲】、【００５４】、【００８２】－【００８３】、【００８７】、【０１０３】、【０１１５】－【０１２３】（ファミリーなし）	1-11, 14-15 12-13
Y	JP 2001-113635 A（王子製紙株式会社）2001.04.24,　【特許請求の範囲】（ファミリーなし）	1-11, 14-15
Y	JP 2006-28439 A（信越ポリマー株式会社）2006.02.02,　【特許請求の範囲】、【００２７】、【００４５】（ファミリーなし）	1-11, 14-15

☐　Ｃ欄の続きにも文献が列挙されている。　　☐　パテントファミリーに関する別紙を参照。

＊　引用文献のカテゴリー
「Ａ」特に関連のある文献ではなく、一般的技術水準を示すもの
「Ｅ」国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの
「Ｌ」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「Ｏ」口頭による開示、使用、展示等に言及する文献
「Ｐ」国際出願日前で、かつ優先権の主張の基礎となる出願の日の後に公表された文献
「Ｔ」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
「Ｘ」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの
「Ｙ」特に関連のある文献であって、当該文献と他の１以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの
「＆」同一パテントファミリー文献

国際調査を完了した日	国際調査報告の発送日
１８．１１．２０１１	２９．１１．２０１１

国際調査機関の名称及びあて先	特許庁審査官（権限のある職員）	４Ｘ	２９３０
日本国特許庁（ＩＳＡ／ＪＰ） 郵便番号１００－８９１５ 東京都千代田区霞が関三丁目４番３号	前田　寛之 電話番号　０３－３５８１－１１０１　内線　３４７７		

様式ＰＣＴ／ＩＳＡ／２１０（第２ページ）（２００９年７月）

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NESPRESSO USA, INC. v. K-FEE SYSTEM GMBH
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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Published:

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

WO 2014/004231 A1

(54) Title: SYSTEMS AND METHODS FOR TREATMENT OF SLEEP APNEA

(57) Abstract: Methods of maintaining airway patency in an airway of a patient. A method includes the steps of wrapping a bioerodable material at least partway around an axis to create a wound bioerodable implant, and coupling two points on the bioerodable material to each other. The invention also provides systems for maintaining airway patency in an airway of a patient that may be used with the methods.

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SYSTEMS AND METHODS FOR TREATMENT OF SLEEP APNEA

INCORPORATION BY REFERENCE

[0001] All publications and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

FIELD

[0002] The disclosure relates to the field of methods and devices for the treatment of airway tissue disorders and more particularly to the treatment of obstructive sleep apnea, and opening the airway of subjects with symptoms of obstructive sleep apnea.

BACKGROUND

[0003] The invention relates to the field of methods and devices for the treatment of airway tissue disorders and more particularly to the treatment of obstructive sleep apnea and opening the airway of subjects with symptoms of obstructive sleep apnea.

[0004] Sleep apnea is defined as the cessation of breathing for ten seconds or longer during sleep. During normal sleep, the throat muscles relax and the airway narrows. During the sleep of a subject with obstructive sleep apnea (OSA), the upper airway narrows significantly more than normal, and during an apneic event, undergoes a complete collapse that stops airflow. In response to a lack of airflow, the subject is awakened at least to a degree sufficient to reinitiate breathing. Apneic events and the associated arousals can occur up to hundreds of times per night, and become highly disruptive of sleep. Obstructive sleep apnea is commonly but not exclusively associated with a heavy body type, a consequence of which is a narrowed oropharyngeal airway.

[0005] Cyclic oxygen desaturation and fragmented sleeping patterns lead to daytime sleepiness, the hallmark symptom of the disorder. Further consequences of sleep apnea may include chronic headaches and depression, as well as diminished facilities such as vigilance, concentration, memory, executive function, and physical dexterity. Ultimately, sleep apnea is highly correlated with increased mortality and life threatening comorbidities. Cardiology complications include hypertension, congestive heart failure, coronary artery disease, cardiac arrhythmias, and atrial fibrillation. OSA is a highly prevalent disease conditions in the United States. An estimated 18 million Americans suffer from OSA to degrees that range from mild to

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severe, many of whom are undiagnosed, at least in part because the afflicted subjects are often unaware of their own condition.

[0006] Treatment of OSA usually begins with suggested lifestyle changes, including weight loss and attention to sleeping habits (such as sleep position and pillow position), or the use of oral appliances that can be worn at night and help position the tongue away from the back of the airway. More aggressive physical interventions include the use of breathing assist systems (such as continuous positive airway pressure machines) that provide a positive pressure to the airway through a mask worn by the subject. In some cases, pharmaceutical interventions can be helpful, but they generally are directed toward countering daytime sleepiness and do not address the root cause. Some surgical interventions are available, such as nasal surgeries, tonsillectomy and/or adenoidectomy, reductions in the soft palate or the uvula or the tongue base, or advancing the tongue base by an attachment to the mandible and pulling the base forward. These surgical approaches can be quite invasive and thus have a last-resort aspect to them and simply do not reliably alleviate or cure the condition. There is a need for less invasive procedures that show promise for greater therapeutic reliability.

[0007] Related devices and methods are described in U.S. 8,167,787, U.S. 2011-0144421, U.S. 2011-0226262, and U.S. Patent Application No. 13/308,449 to Gillis et al. filed November 30, 2011 the disclosures of which are incorporated herein by reference.

SUMMARY OF THE DISCLOSURE

[0008] The present invention provides methods and devices for treating obstructive sleep apnea, other sleep disorders, other airway problems or airway disorders, other jaw or throat problems or disorders such as snoring, other sleep-disordered breathing, other breathing difficulties, swallowing difficulties, or speech problems. Embodiments of the invention include methods for opening a collapsed or obstructed airway with devices that can be implanted into various tissues that form the airway. Embodiments of the devices include resiliently deformable materials and bioerodable materials. The deformable portion of the devices may be formed into a preferred shape and may then subsequently be deformed and stabilized in that deformed shape by incorporation or application of bioerodable materials to create a device in an implantable form. Once implanted into a tissue site, and thus exposed to an aqueous environment and to cellular and enzymatic action, the bioerodable portions of the device erode, thereby allowing the deformable portion of the device to return toward an at-rest form. Embodiments of the method, in their simplest form, thus include implanting a device, the bioerodable portion of the device bioeroding, the device changing shape as a consequence of the bioeroding, and the tissue remodeling in accordance with the force being exerted by the shape changing of the device.

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[0009] One aspect of the invention provides a method of maintaining airway patency in an airway of a patient. The method includes the steps of implanting a device into airway-forming tissue without affixing the device to the tissue and permitting a bioerodable portion of the device to bioerode to apply a force to the airway-forming tissue to maintain airway patency. In some embodiments, the method also includes the step of expanding a portion of the device without affixing the device to the tissue, such as by, for example, permitting the portion of the device to self-expand. In various embodiments, the implanting step may include the step of inserting the device into the patient submandibularly, sublingually, and/or intra-orally.

[00010] In some embodiments, the permitting step includes the step of changing a shape of the device when the bioerodable portion bioerodes, such as by changing a length, curvature and/or width of the device. The method may also include the step of permitting newly formed tissue to infiltrate the device, possibly with the newly formed tissue at least partially infiltrating the device prior to applying a force to the airway-forming tissue.

[00011] In various embodiments, the implanting step includes the step of inserting the device into tongue tissue, soft palate tissue, pharyngeal wall tissue and/or epiglottis tissue. The method may also include the step of releasing a bioactive agent from the bioerodable portion as it bioerodes.

[00012] Another aspect of the invention provides a device for maintaining patency of an airway of a patient. In some embodiments, the device has a body having an at-rest shape and a deformed shape, the body being adapted to be implanted into airway-forming tissue of the patient, and proximal and distal anchors adapted to be implanted into the airway-forming tissue, without affixing the device to the tissue, and to be infiltrated by tissue to affix the anchors to the airway-forming tissue, with at least one bioerodable element maintaining the body in the deformed shape against a return force and the body being configured to return toward the at-rest shape upon erosion of the bioerodable element. In various embodiments, the body is sized and shaped to be inserted into tongue tissue, into soft palate tissue, and/or into pharyngeal tissue.

[00013] In various embodiments, the bioerodable element includes a coil and/or a C-shaped element. In some embodiments, at least one of the proximal and distal anchors is adapted to expand, possibly through self-expansion. One or more of the anchors may contain woven and/or non-woven material and may include through-holes to permit tissue in-growth. One or more of the anchors may also contain braided material.

[00014] In some embodiments, the device's deformed shape is longer, straighter and/or wider than its at-rest shape. The device may also have an elutable bioactive agent in some embodiments.

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[00015] Another aspect of the invention provides an implant system for treating a sleep disorder including a bioerodable material and an elongate long term implant, the bioerodable material at least partially enveloping the elongate long term implant and resisting a compressive force of the long term implant, the bioerodable material including a first region having a first flexibility and a second region having a second flexibility that is less than the first flexibility. In some embodiments, the implant system includes a plurality of first regions having the first flexibility and a plurality of second regions having the second, lesser flexibility. In some embodiments, the second regions of lesser flexibility are configured to maintain the bioerodable material in an enveloping configuration relative to the elongate long term implant. In some embodiments, the regions of lesser flexibility are configured to substantially hold the bioerodable material in an initial shape for a period of time that is less than 16 weeks upon exposure to a body fluid (e.g. between 2 and 6 weeks or between 3 and 5 weeks).

[00016] In some embodiments, the bioerodable material includes a spring having a plurality of coils, and the first regions having the first flexibility include two coils of the spring.

[00017] In some embodiments, the second regions having the second, lesser flexibility include two points on the coils that are linked with each other.

[00018] In some embodiments, the elongate long term implant comprises a silicone material. In some embodiments, the bioerodable material includes a polymer based on lactic acid (e.g. poly(lactic acid) or poly(DL-lactic-co-glycolic acid)).

[00019] Another aspect of the invention provides an implant system for implanting in airway forming tissue including a bioerodable material and an elongate long term implant, the bioerodable material at least partially enveloping the elongate long term implant and linked between a first set of two points on the bioerodable material to form a first bridge. In some embodiments, the bioerodable material is configured to hold the elongate long term implant in an initial shape (e.g. a tensioned state).

[00020] In some embodiments the bioerodable material includes a spring having at least two coils and a plurality of points, and the first bridge connects two points on the spring. In some embodiments, the two points are on different coils at a first end of the spring. In some embodiments, the bioerodable material is linked between a second set of two points on a second set of coils of the spring to form a second bridge. In some of these embodiments the second set of coils is at a second end of the spring. In some of these embodiments, the first and second bridges are bioerodable.

[00021] In some embodiments, substantially each coil is linked to at least one other coil to form a plurality of bridges.

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[00022] Yet another aspect of the invention provides a resilient elongate implant body having a first insertion shape and a second therapeutic shape, and a bioerodable material having two coils that at least partially envelop the resilient elongate implant body, and the coils are coupled together to form a coupled coil structure. In some embodiments, the bioerodable material is configured to hold the implant body in the initial insertion shape. In some of these embodiments, the bioerodable material includes additional coils continuous with the two coils to form a spring and the additional coils of the spring are wrapped around the implant body, and the two coils are at an end of the spring. In some of these embodiments, substantially each coil is coupled to at least one other coil.

[00023] Yet another aspect of the invention provides a method of manufacturing an implant system, the implant having an elongate implant body and a bioerodable support material configured to hold the elongate implant body in a first, elongate shape, the method including the steps of wrapping the bioerodable support material at least partway around the implant body, the bioerodable support material having two points on it, and coupling the two points with each other to create a coupled bioerodable support material.

[00024] Yet another aspect of the invention includes a method of manufacturing a bioerodable implant including the steps of wrapping a bioerodable material at least partway around an axis to create a wound bioerodable implant, the bioerodable material including two points, and coupling the two points to each other. In some embodiments, the wound bioerodable implant includes a helix and coupling includes heating the helix to fuse the two points.

[00025] In some embodiments, the axis includes an elongate long term implant, and the wrapping around an axis comprises wrapping the bioerodable material around the elongate long term implant to create an implant system. In some of these embodiments, the method includes applying an expansive force to the elongate long term implant with the bioerodable material to hold the long term implant in an initial shape.

[00026] In some embodiments, the coupling step includes attaching a bioerodable material to the two points to create a support strut. In some embodiments, the coupling step includes applying at least one of an adhesive, an other chemical, or an energy source to the bioerodable material. In some embodiments, the coupling step includes heating the bioerodable material to melt the two points together.

BRIEF DESCRIPTION OF THE DRAWINGS

[00027] The novel features of the invention are set forth with particularity in the claims that follow. A better understanding of the features and advantages of the present invention will be obtained by reference to the following detailed description that sets forth illustrative

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embodiments, in which the principles of the invention are utilized, and the accompanying drawings of which:

[00028] FIG. 1 shows an overview of the healthy human airway anatomy, with particular attention to the nasopharyngeal, oropharangeal, and hypopharyngeal regions.

[00029] FIG. 2 provides a view of a compromised airway, with an occlusion in the oropharyngeal region due to posterior slippage of the base of the tongue and a thickened posterior pharyngeal wall.

[00030] FIG. 3 provides a view of a compromised airway, with an occlusion in the nasopharyngeal region due to posterior slippage of the soft palate.

[00031] FIG. 4 provides a view of a compromised airway, with an occlusion in the oropharyngeal region due to posterior slippage of the base of the tongue and the soft palate, a thickened posterior pharyngeal wall, and posterior flopping of the epiglottis.

[00032] FIGS. 5A-C show an airway-maintaining device according to one embodiment of the invention.

[00033] FIGS. 6A-B show an airway-maintaining device according to another embodiment of the invention. FIG. 6B is an enlarged cross-section along the lines shown in FIG. 6A.

[00034] FIGS. 6C-D show an airway-maintaining device according to yet another embodiment of the invention. FIG. 6D is an enlarged cross-section along the lines shown in Figure 6C.

[00035] FIGS. 6E-F show an airway-maintaining device according to still another embodiment of the invention. FIG. 6F is an enlarged cross-section along the lines shown in Figure 6E.

[00036] FIGS. 6G-H show an airway-maintaining device according to another embodiment of the invention. FIG. 6H is an enlarged cross-section along the lines shown in Figure 6G.

[00037] FIGS. 6I-J show an airway-maintaining device according to yet another embodiment of the invention. FIG. 6J is a cross-section along the lines shown in FIG. 6I.

[00038] FIGS. 7A-C show implantation and use of an airway-maintaining device delivered submandibularly.

[00039] FIGS. 8A-C show implantation and use of an airway-maintaining device delivered intraorally and sublingually.

[00040] FIGS. 9A-C show implantation and use of an airway-maintaining device delivered intraorally to the soft palate.

[00041] FIGS. 10A-C show details of the device shown in FIGS. 9.

[00042] FIGS. 11A-B show details of the device shown in FIGS. 9 and 10 in place in the soft palate.

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[00043] FIGS. 12A-B show an airway maintaining device according to yet another embodiment of the invention in place in the patient.

[00044] Figure 13 is a graph comparing tensile force applied by embodiments of the invention and theoretical force applied by other obstructive sleep apnea therapy devices.

[00045] FIGS. 14A-C show an airway-maintaining device according to still another embodiment of the invention.

[00046] FIGS. 15A-B show the device of FIGS. 14 in place in patient.

[00047] FIGS. 16A-B show the devices of FIGS. 8 and 9 in place in a patient.

[00048] FIGS. 17A-C show multiple devices of FIGS. 8 and 9 in place in a patient.

[00049] FIGS. 18A-C show another embodiment of the airway maintaining device of this invention.

[00050] FIGS. 19 A-B show two views of an embodiment of a device or implant system with a bioerodable material around an elongate long-term implant.

[00051] FIGS. 19 C-D show two views of a device, such as that shown in FIGS. 19 A-B, after foreshortening.

[00052] FIGS. 20A-B show two views of a device that has prematurely foreshortened.

[00053] FIG. 21 shows a method of coupling a bioerodable material to itself to form a bridge according to one aspect of the invention.

[00054] FIGS. 22 A-C show two versions of a device with (FIGS. 22 A-B) and without (FIG. 22 C) coupling.

[00055] FIG. 23 A, B shows two views of a device with cuff or C-shaped portion partially enveloping a long term implant portion and connected by a bridge.

[00056] FIG. 24 shows an implant system with a modular design.

[00057] FIG. 25 shows a ribbon-like structure wrapped around a long term implant and coupled to itself.

[00058] FIG. 26 shows an embodiment of a device with a self-linking bioerodable portion.

[00059] FIG. 27 shows an embodiment of a device with a stent-like structure holding the long term portion. FIGS. 28 and 29 show embodiments of devices with regions of greater flexibility and regions of lesser flexibility.

[00060] FIG. 30 shows an embodiment of a device with minimal wrapping of the bioerodable portion around the long term implant portion.

[00061] FIG. 31 shows another embodiment of a device with a single spring coupled to itself.

[00062] FIG. 32 shows another embodiment of a device according to the invention with the bioerodable portion coupled with the long-term elongate implant portion.

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[00063] FIG. 33 depicts an end portion of an alternative revisable implant including a cut wire for cutting a tissue plug.

[00064] FIG. 34 is a cut-away view depicting the implant of FIG. 14 in a tissue site in the process of actuating the cut wire.

[00065] FIG. 35 depicts an end portion of an alternative revisable implant including a cut wire for cutting a plurality of tissue plugs.

[00066] FIGS. 36A-36B depict other embodiments of implant bodies configured with axially inelastic anchoring end portions and an elastic medial portion, wherein the end portions have a substantial axial length relative to the medial portions.

[00067] FIG. 37 is an enlarged view of an anchoring end of the implant body of FIG. 36B depicting non-stretchable interior elements.

[00068] FIGS. 38 A-D show implant length over time after implant placement in the tongue or soft palate.

DETAILED DESCRIPTION

[00069] FIG. 1 is a sagittal view of the structures that form the pharyngeal airway 4. One or more of these structures can become compromised under various conditions to the extent that it (they) obstructs or occludes passage of air through airway 4 and thus contributes to obstructive sleep apnea. These or other causes may contribute to other sleep disorders, other airway problems or airway disorders or jaw or throat problems or disorders and may include snoring, other sleep-disordered breathing, other breathing difficulties (during sleep or wakefulness, difficulty swallowing, or speech problems. The pharynx is divided, from superior to inferior, into the nasopharynx 1, the oropharynx 2 and the hypopharynx 3. Variations of FIG. 1 are provided in FIGS. 2, 3, and 4, which depict airway obstruction sites 5 at various levels in the pharyngeal airway. FIG. 2, for example, shows an occlusion 5 at the level of the oropharynx 2, where the base of the tongue 16 and a thickened posterior pharyngeal wall 22 have collapsed against each other. FIG. 3 shows an occlusion 5 at the level of the nasopharynx 1, where an elongated and/or floppy soft palate 6 has collapsed against a thickened posterior pharyngeal wall 22. FIG. 4 shows an occlusion 5 at the level of the oropharynx and nasopharynx 1 and 2, where both an elongated soft palate 6, base of tongue 16 and a floppy epiglottis 12 have collapsed against the pharyngeal wall 22.

[00070] With reference to FIGS. 1-4, the nasopharynx 1 is the portion of the pharynx at the level or above the soft palate 6. In the nasopharynx, a deviated nasal septum or enlarged nasal turbinates 10 may occasionally contribute to upper airway resistance or blockage. Rarely, a nasal mass, such as a polyp, cyst or tumor may be a source of obstruction. The oropharynx 2

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includes structures from the soft palate 6 to the upper border of the epiglottis 12 and includes the inferior surface of the hard palate 14, tongue 16, tonsils 18, palatoglossal arch 20, the posterior pharyngeal wall 22 and the mandible 24. The mandible typically has a bone thickness of about 5 mm to about 10 mm anteriorly with similar thicknesses laterally. An obstruction in the oropharynx 2 may result when the tongue 16 is displaced posteriorly during sleep as a consequence of reduced muscle activity during deep or non-REM sleep. The displaced tongue 16 may push the soft palate 6 posteriorly and may seal off the nasopharynx 1 from the oropharynx 2. The tongue 16 may also contact the posterior pharyngeal wall 22, which causes further airway obstruction.

[00071] The hypopharynx 3 includes the region from the upper border of the epiglottis 12 to the inferior border of the cricoid cartilage 14. The hypopharynx 3 further includes the hyoid bone 28, a U-shaped, free-floating bone that does not articulate with any other bone. The hyoid bone 28 is attached to surrounding structures by various muscles and connective tissues. The hyoid bone 28 lies inferior to the tongue 16 and superior to the thyroid cartilage 30. A thyrohyoid membrane 17 and a thyrohyoid muscle 18 attaches to the inferior border of the hyoid 28 and the superior border of the thyroid cartilage 30. The epiglottis 12 is infero-posterior to the hyoid bone 28 and attaches to the hyoid bone by a median hyoepiglottic ligament. The hyoid bone attaches anteriorly to the infero-posterior aspect of the mandible 24 by the geniohyoid muscle.

[00072] The invention provides a method of and devices for maintaining airway patency in an airway of a patient by implanting one or more devices into airway-forming tissue and permitting a bioerodable portion of the device to bioerode, thereby applying a force to the airway-forming tissue to maintain airway patency due to, e.g., a curvature, length or width change in the device. The method may be used and/or a device may be implanted to treat a sleep disorder, snoring or any other disorder, condition or disease or to otherwise alter a shape or response of a tissue. In some embodiments, the device or devices are implanted without initially affixing the device to the tissue. Over time, tissue growth or ingrowth into the devices may provide some fixation of the devices to the airway-forming tissue prior to the bioerosion and the device shape change. Various embodiments of shape-changing implants may be used to practice the invention, and the devices may be implanted into various parts of the patient's airway-forming tissue and for various reasons, as needed.

[00073] FIGS. 5A-C show one embodiment of a device 500 that may be implanted in airway-forming tissue to maintain patency of the patient's airway. Device 500 has a body 502 with a plurality of narrow sections 504 separated by wide sections 506. As shown, the narrow and wide sections are cylindrical, although other shapes may be used. The body 502 may be made of a resiliently deformable material, such as silicone rubber, polyurethanes or other resiliently

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deformable polymer or a coil of stainless steel, spring steel, or superelastic nickel-titanium alloy or other resiliently deformable metal, or a composite of the resiliently deformable polymer and metal.

[00074] FIG. 5B shows body 502 in its at-rest shape. In FIG. 5A, body 502 has been stretched to a deformed shape. Spacers 508 formed from a bioerodable or bioabsorbable material (such as, e.g., polycaprolactone, polylactic acid, polyglycolic acid, polylactide coglycolide, polyglactin, poly-L-lactide, polyhydroxalkanoates, starch, cellulose, chitosan, or structural protein) have been inserted between wide sections 506 to maintain the device in its deformed shape. In this embodiment, the spacers 508 are injection molded and have a C shape, although other manufacturing techniques and other shapes may be used as desired.

[00075] Anchors 510 are formed at both ends of body 502. In this embodiment, anchors 510 are formed from a non-woven fabric (such as polypropylene, polyethylene, or polyester) to promote tissue ingrowth. Other anchors may be used, as desired.

[00076] Device 500 may be implanted in a patient's airway-forming tissue in the deformed shape shown in FIG. 5A. In some embodiments, the device 500 is not affixed to the airway-forming tissue when implanted. Over time, tissue may grow into the fabric of anchors 510 to at least partially affix the device to the airway-forming tissue. Also over time, the bioerodable spacers 508 will bioerode, thereby permitting device 500 to move back toward the at-rest form shown in FIG. 5A. As it attempts to return to its at-rest shape, device 500 exerts a force on the airway-forming tissue into which it is implanted to maintain the patient's airway in a patent condition.

[00077] FIGS. 6A-J show various other embodiments of the invention in their deformed states. As in the embodiment of FIGS. 5, these devices for maintaining patency of an airway may be implanted into airway-forming tissue of the patient in the illustrated deformed state. Over time, tissue may grow into the device anchors and possibly other parts of the device to at least partially affix the device to the airway-forming tissue. Also over time, the bioerodable spacer portions of the device may bioerode, thereby permitting the device to attempt to move toward a shorter at-rest shape, thereby exerting a force on the airway-forming tissue into which it is implanted to maintain the patient's airway in a patent condition. The deformable bodies of these devices may be formed, e.g., of silicone rubber.

[00078] In FIGS. 6A-B, device 600 has a stiff bioerodable fiber 608 helically wound within narrow sections 604 of a resiliently deformable body 602 between wide sections 606 to maintain body 602 in its stretched deformed state. Fiber 608 may be made, e.g., of polyglactin 910, which is a copolymer of 90% glycolide and 10% L-lactide. When fiber 608 bioerodes, body 602 will attempt to shorten to its at-rest shape. Anchors 610 are disposed at both ends of body 602.

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Anchors 610 may be formed from woven polyester, polyethylene or polypropylene to provide for tissue ingrowth.

[00079] FIGS. 6C-D show a device 611 having a resiliently deformable body 612 in which a plurality elongated openings 614 are formed. In the depicted deformed state, bioerodable, rod shaped, spacers 618 (formed from, e.g., polylactidecoglycolide (PLG)) are disposed in the openings 614 to maintain the body's elongated deformed shape. Paddle-shaped anchor regions 620 having a plurality of holes or depressions 619 are disposed at both ends of body 612. Holes or depressions 619 permit tissue in-growth. Anchor regions 620 may be integral with the central portion of body 612 or may be formed from a different material, such as reinforced polyester. Anchor regions also may be integral with the central portion of body 612 and contain a composite reinforcing element such as a polyester fabric.

[00080] FIGS. 6E-F show a device 621 similar to that shown in FIGS. 5A-C in which the bioerodable portion 628 is formed of a helically wound bioerodable fiber, such as that discussed above with respect to FIGS. 6A-B and contains anchoring regions 630 of non woven fabric (e.g. polyester, polyethylene, or polypropylene).

[00081] FIGS. 6G-H show a device 631 having a resiliently deformable body 632 similar to body 602 of FIG. 6A. As shown, body 632 is in a stretched deformed shape. Bioerodable spacers 638 (similar to those of the embodiment shown in FIG. 5A) are disposed in narrow portions 634 between wide portions 636 to maintain body in this stretched shape. Anchors 640 on both ends are formed from an open or closed cell foam material to promote tissue in-growth.

[00082] FIGS. 6I-J show a device 641 substantially the same as the device shown in FIGS. 6E-F with the exception of the anchors 649 and 650. In this embodiment, anchors 649 and 650 are self-expanding baskets that can be compressed to the form shown as anchor 650 during implantation and will self-expand toward the at-rest shape shown as anchor 649 after deployment. The open areas of the anchors provide material loops and spaces for tissue ingrowth and attachment.

[00083] Other embodiments of the airway maintaining device may use various aspects of the illustrated embodiments as needed. For example, the anchors at end of the device body may differ from each other.

[00084] FIGS. 7-9 illustrate therapy provided by embodiments of this invention. In FIGS. 7A-C, a delivery tool 702 has been inserted submandibularly into the patient 700 to deliver an airway maintaining device 710 into a region of the patient's tongue 704 forming part of the patient's airway 708, which is shown as being blocked in FIG. 7A. Device 710 may be, e.g., any of the devices discussed above with respect to FIGS. 5 and 6. As shown in FIG. 7B, the device 710 is delivered in an elongated deformed state. In some embodiments, device 710 when first

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delivered is not affixed to the tongue tissue. Over time, however, tissue may grow into the anchors 711 of device 710 and/or other parts of the device. Also over time, bioerodable portions 712 of device 710 will bioerode, thereby permitting device 710 to move toward a shorter at-rest shape, thereby applying a force to the patient's tissue to maintain the patency of the airway, as shown in FIG. 7C.

[00085] In FIGS. 8A-C, a delivery tool 802 has been inserted intraorally and sublingually into the patient 800 to deliver an airway maintaining device 810 into a region of the patient's tongue 804 forming part of the patient's airway 808, which is shown as being blocked in FIG. 8A. Device 810 may be, e.g., any of the devices discussed above with respect to FIGS. 5 and 6. As shown in FIG. 8B, the device 810 is delivered in an elongated deformed state. In some embodiments, device 810 when first delivered is not affixed to the tongue tissue. Over time, however, tissue may grow into the anchors 811 of device 810 and/or other parts of the device. Also over time, bioerodable portions 812 of device 810 will bioerode, thereby permitting device 810 to move toward a shorter at-rest shape, thereby applying a force to the patient's tissue to maintain the patency of the airway, as shown in FIG. 8C.

[00086] In FIGS. 9A-C, a delivery tool 902 has been inserted intraorally into the patient 900 to deliver an airway maintaining device 910 into a region of the patient's soft palate 904 forming part of the patient's airway 908, which is shown as being blocked in FIG. 9A. Device 910 is described in further detail below with respect to FIGS. 10 and 11. As shown in FIGS. 9B and 11A, the device 910 is delivered in an elongated and straightened deformed state. In some embodiments, device 910 when first delivered is not affixed to the soft palate tissue. Over time, however, tissue may grow into the anchors 920 of device 910 and/or other parts of the device. Also over time, bioerodable portions 918 of device 910 will bioerode, thereby permitting device 910 to move toward a shorter and more curved at-rest shape, thereby applying a force to the patient's soft palate tissue to maintain the patency of the airway, as shown in FIGS. 9C and 11B.

[00087] FIGS. 10A-C and 11A-B show more details of an airway-maintaining device 910 suitable for implantation in the soft palate. The device's deformed shape is shown in FIGS. 10A and 11A. In this shape, spacers 918 formed from a bioerodable material are disposed in narrow regions 914 of body 912 between wide regions 914 of body 912. Body 912 is formed from a resiliently deformable material (such as, e.g., silicone rubber, polyurethanes or other resiliently deformable polymer or a coil of stainless steel, spring steel, or superelastic nickel-titanium alloy or other resiliently deformable metal, or a composite of the resiliently deformable polymer and metal.) and is deformed into the straight and elongated form shown in FIGS. 10A and 11A. The shorter and more curved at-rest shape of body 912 is shown in FIG. 10B. This is the shape the device will attempt to return to after the bioerodable portions 916 bioerode, thereby exerting

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force on the airway-forming tissue of the soft palate, as shown in FIG. 11B. In this embodiment, anchors 920 are formed from a non-woven fabric (such as polypropylene or polyester) to promote tissue ingrowth. Other anchors may be used, as desired. In this embodiment, the spacers 918 are injection molded from polycaprolactone, polylactic acid, polyglycolic acid, polylactide coglycolide, polyglactin, poly-L-lactide and have a C shape, although other manufacturing techniques (e.g., dipping processes for applying the spacers over the resiliently deformable polymer or metal), materials, and other shapes may be used as desired.

[00088] FIGS. 12A-B show another embodiment of an airway maintaining device 1200 implanted submandibularly into tongue tissue 1201 forming part of the patient's airway. Device 1200 has anchors 1202 and 1204 which differ from each other. Anchor 1204 is an expandable anchor, such as the self-expandable anchor 649 described above with respect to FIG. 6I, whereas anchor 1202 is not expandable. As shown in FIG. 12A, device 1200 when implanted into tissue 1201 is in an elongated deformed shape. Over time, bioerodable portions 1206 of device 1200 will bioerode, and device 1200 will attempt to return to its shorter at-rest shape, thereby exerting a force on tissue 1201 to maintain the patency of airway 1208, as shown in FIG. 12B.

[00089] FIG. 13 is a graph comparing theoretical average tensile force provided to patient airway-forming tissue by various implantable obstructive sleep apnea therapy devices respect to the amount of stretching experienced by the implant. Tether devices are shown by the two lines formed by the square data points. As can be seen, such rigid devices provide no tensile force on the patient's tissue until all slack has been removed, at which point the tether provides a nearly infinite force, possibly exceeding the patient's tolerance limit.

[00090] The curve formed by the round data points show theoretical tensile force applied by magnet-based obstructive sleep apnea implants. As can be seen, such devices have a very narrow operational range falling with the therapeutic range providing a benefit to the patient through the application of a minimum therapeutic force.

[00091] The curves formed by the diamond and cross data points show theoretical tensile forces applied by two airway-maintaining devices according to this invention having two different spring constants in their deformable device bodies. As shown, these devices can be designed so that they provide beneficial airway maintenance therapy to the patient over a wide range of lengths.

[00092] FIGS. 14A-C and15A-B show yet another embodiment of the invention. Device 1400 has a device body with two elongate rails 1402 and 1404 formed from a resiliently deformable material, such as silicone rubber. A plurality of spaced-apart oval flanges 1406 are attached to rails 1402 and 1404. In the deformed state shown in FIGS. 14A and 15A, C-shaped

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bioerodable spacers 1408 are disposed between adjacent flanges 1406 to maintain the device in its elongated shape. When spacers 1408 bioerode over time, device 1400 moves toward the at-rest shape shown in FIG. 14B, thereby exerting a force on the patient's airway forming tissue (shown as the tongue 1410 in FIGS. 15) to maintain patency of the airway 1412 as shown in Figure 15B.

[00093] FIGS. 16A-B demonstrate how multiple airway-maintaining devices may be implanted into a single patient, such as the tongue device 810 and the soft palate device 910 described with respect to FIGS. 8 and 9 above, respectively.

[00094] Likewise, FIGS. 17A-C show how multiple airway-maintaining devices may be implanted into the same region of airway-forming tissue.

[00095] FIGS. 18 A-C show an embodiment of an airway-maintaining device 1800 in which the deformed state of the device body 1802 shown in FIG. 18A is both longer and wider than the at-rest state of the device body 1802 shown in FIG. 18B. Bioerodable spacers 1802 are disposed in openings 1804 formed in resiliently deformable body 1802. As the spacers erode, the body 1802 will move toward its at-rest shape. The openings in the deformed and at rest shapes 1804 and 1806 constitute anchoring elements. This embodiment could be placed in an anatomical structure such as the soft palate and could exert force on the airway forming tissue in two directions to maintain patency.

[00096] In some embodiments, the device may include one or more bioactive agents in the bioerodable portion(s). Bioactive agents such as drugs or hormones that are eluted during the course of erosion of the bioerodable materials, may serve, for example, to promote healing of the implant wound, or to promote stabilization of the implanted device within the tissue site by, for example, promoting the toughening the fibrotic tissue capsule that forms around the implanted device.

[00097] FIGS. 19A-D show an embodiment of the invention similar to the devices shown in FIGS. 6A-J with long term elongate implant portion 114 shown without a bioerodable material portion (FIGS. 19 C-D) and implant system 100 shown with bioerodable portion 110 at least partially enveloping the long term elongate implant portion of the device (FIGS. 19 A-B). In this example, the bioerodable portion is helically wound around the elongate implant. Bioerodable portions 110 are adjacent or connected with wide sections 108 of the long-term implant and may be configured to resist a compressive force from the long term implant or to apply an expansive force to the long term implant. The long term implant may be made of a resiliently deformable material, such as a silicone material (e.g. silicone rubber), polyurethane or other resiliently deformable polymer or a coil of stainless steel, spring steel, or superelastic nickel-titanium alloy or other resiliently deformable metal, or a composite of the resiliently deformable polymer and

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metal. In particular, when placed in an animal's body, one or more bioerodable portions 110 may hold the elongate implant in a first, elongated shape until the implant is anchored to an airway tissue, such as by a fibrotic response or tissue growth through one or more holes 106 in anchor end(s) 104. Over time, the bioerodable material bioerodes, the device shortens and exerts a therapeutic force on airway tissue. Compare the relative compositions, shapes, and lengths of foreshortened device 114 (FIGS. 19C-D), having exposed narrow sections 116 after bioerosion, with device 100 (FIGS. 19A-B) before substantial bioerosion has taken place and having bioerodable material 110 partially enveloping the long-term implant.

[00098] It may be beneficial for a device to remain in an elongated shape until substantial or sufficient tissue growth has taken place and the ends of the device are anchored into airway tissue. However, in some conditions a device might not maintain a sufficiently elongated, (stretched) configuration as shown in FIGS. 19A-B for a period of time sufficient to allow tissue to anchor the implant into tissue (e.g. to anchor the implant so that it can exert a desired therapeutic force on the tissue). Rather, if the implant shortens too much from its first, elongated shape before becoming anchored in tissue (or does not become anchored), it may not be capable of exerting sufficient force on airway tissue to have a therapeutic effect. Some specific devices, similar to those shown in FIGS. 19 A-B, when tested in an animal model, did not exhibit the desired tissue effect. It is hypothesized that normal airway tissue movement imposed mechanical forces on the devices that led to premature device foreshortening. See Example 2. In particular, in vitro testing showed that one explanation for the lack of the desired tissue effect could be premature long-term implant foreshortening due to mechanical agitation causing its premature release from the bioerodable material that otherwise holds it in an elongated configuration (shape). When implant systems were subject to ultrasound vibration in a saline bath (to model or mimic the implant environment in a body), coiled bioerodable material, such as that shown in FIGS. 19A-B, unwound relative to the long-term implant axis. See Example 2. FIGS. 20 A-B show an example of an implant, such as the one depicted in FIGS. 19A-B, in which coils including end coil 124 at an end of bioerodable helix 122 on device 120 have unwound and part of wide section 126 of the long term implant has retracted inside the end coils. The coils remaining wound around the narrow long term implant portion may not be able to provide a sufficient resistive force to hold the long term implant in a desired, elongated configuration (shape). Therefore, it may sometimes be beneficial to create, reinforce or change a device structure such that it will substantially hold a desired shape in vivo for a sufficient period of time (e.g. in the presence of mechanical or other forces) to allow tissue anchoring of the device to take place. Either a bioerodable or a long term implant portion (or both) may be configured or altered to improve the ability of the long term implant to be placed and to remain in a tensioned shape

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(e.g. held by the bioerodable portion) until sufficient tissue growth has taken place. An initial tensioned shape or configuration may be any shape or configuration that creates a tension between a bioerodable material and a long-term implant that is different from a final shape or configuration (in which the bioerodable material has bioeroded and no longer exerts a tension on the long term implant). Alternatively, an additional piece (such as a holder or clip) may hold the bioerodable portion or long term implant in a preferred shape or configuration.

[00099] In some embodiments, an implant system according to the disclosure includes a resilient elongate implant body having a first insertion shape and a second therapeutic shape and a bioerodable material including at least two coils that at least partially envelop the resilient elongate implant body, wherein the coils are coupled together to form a coupled coil structure. A therapeutic shape of an elongate implant body may be a shape that the body takes after a bioerodable portion bioerodes. A therapeutic shape may be a shape configured to exert a desired force) on a target tissue (e.g. an airway forming tissue).

[000100] A bioerodable portion may be manufactured to better maintain an initial or desired shape, for example, by changing the way the bioerodable material is otherwise held in place relative to the resilient or elongate long term implant. The bioerodable portion may be held in position along the elongate implant in any way. For example, the portion may be held using a chemical coupling and/or using a mechanical coupling (e.g. an interlocking). To aid in device performance, including maintaining a device shape, portions of the bioerodable implant may be made less flexible compared with other, more flexible sections. The less flexible portions may hold the implant in a first shape and prevent the bioerodable portion from undergoing undesired movement (e.g. unwinding) relative to the long term implant. A point on an implant may be made less flexible, for example, by coupling one portion of a bioerodable material to another portion of the bioerodable material (e.g. coupling to itself). In one embodiment, two points on the bioerodable portion may be fused together. The two points may be on the same coils or may be on different coils. FIG. 21 shows two coils on bioerodable helix 132 of implant 130 fused at fusion point or bridge 137 at a first end to bridge a first region. The bridge may create a region of lesser flexibility on the bioerodable portion, reducing movement of the bioerodable implant, and thereby maintaining the bioerodable material in an enveloping configuration relative to the long term implant. A point connecting a coil and a bridge has lesser flexibility than a flexibility of a (or either) coil to which it is coupled. Any number (or no) bridges may be made on a bioerodable portion. A bridge may have a different flexibility.

[000101] In one particular embodiment, a point on a coil may be fused to another point on the same coil.

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[000102] In some embodiments, coils may be fused at both ends of a bioerodable portion. Figure 21 shows two coils fused at a first bridge 137 and a second bridge 138 at a second end of the bioerodable portion. Fusing or anchoring both ends of a bioerodable portion may prevent a bioerodable implant from rotating or unwinding relative to the long term implant.

[000103] In another embodiment, two other coils may be fused to form a third bridge 136. The third bridge may be anywhere along the bioerodable portion, but in one particular example it is near the middle of a bioerodable portion. The third bridge may, for example, provide additional strength to the bioerodable portion to resist movement caused by mechanical agitation from airway tissue movement and may serve as a backup in the event that one of the first two bridges near an end of the bioerodable portion prematurely breaks while implanted (e.g. breaks before tissue growth has anchored the implant) such that the breakage might otherwise allow the bioerodable portion to unwind and the long term implant portion to prematurely foreshorten. A fourth, fifth, sixth, seventh, eighth or more bridges may be formed. In some embodiments, there may be a bridge at least every 1 mm, every 2 mm, every 3 mm, every 4 mm, every 5 mm, every 10 mm, or every 15 mm. In some embodiments, each coil may be fused to at least one (or at least two) other coil(s). In some embodiments, each coil may be linked to at least one other coil, forming a plurality of bridges. In one particular embodiment, all of the coils are fused together. An implant may have one, two, three or more than three separate bioerodable portions. Any (some, or all) of a bioerodable portion(s) may be fused to itself or one (or more) bioerodable portion(s) may be fused to one or more other bioerodable portion(s).

[000104] The bioerodable material may be linked or fused to itself in any way. The points on the material may be fused using a source that can generate energy (heat). The energy (heat) may melt a portion of the bioerodable material to cause it to bind to another portion of the bioerodable material and remain bound after cooling. The heat source may be a direct heat source (such as a soldering iron) that is at a temperature higher than an implant temperature or the heat source may be an indirect source such as a chemical source or light source, vibrational welding, induction welding, ultrasonic welding, or radiofrequency welding source that causes heat to be generated in the implant.

[000105] Instead, or in addition to a bioerodable material melting or otherwise linking to itself, a bioerodable material may be coupled to itself using an additional joining material such as an adhesive that bonds or a solvent that bonds by melting adjacent surfaces together or small clip or mechanical attachment to form a bridge and couple two (or more) points on the material. FIGS. 22A, C show implant 140 with bioerodable material in the form of helix 142. Bar (or bridge) 144 connects essentially all of the coils of a bioerodable portion, creating a support strut that may help hold the helix in an initial shape. The support strut may create a point(s) or region(s) of

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reduced flexibility on the helix and the helix may then resist movement from airway tissue and therefore maintain an elongated shape until tissue growth has anchored the implant (e.g. to create a biological anchor). An end of the helix opposes wide section 150 of the long term implant to thereby hold the long term implant in an elongated configuration. Compare the coils of the helix and the relative length of implant 140 with bar 144 in place along the coils in FIGS. 22 A, C with a foreshortened bioerodable helix, the unwound coils 121 and relative length of implant 120 without a support strut shown in FIG. 22B. The bioerodable portion in implant 120 did not resist a compressive force from the long term implant, and the long term implant prematurely shortened. A bar may connect essentially all of the coils of a helical portion together, as shown in FIG. 22A, C. Additionally, a second (or more than two) bar(s) may be placed along the helix to create additional regions of reduced flexibility, provide additional support, and reduce relative rotational movement of the helix.

[000106] Although any two (or more) coils may be connected by a bar, it may be especially useful to couple end coils, such as coils 146, 148, as shown in FIG. 22C to prevent rotation of the helix around the axis while maintaining device flexibility. In some embodiments, a first bar may be placed at a first end of a helix to connect a first set of end coils, and a second bar may be placed at a second end of a helix to connect a second set of end coils. In another embodiment, an additional bar(s) may be placed along two non-end coils to provide additional support, such as for backup in case one of the end bars breaks prematurely.

[000107] A support structure between two (or more) portions of a bioerodable material may be any material that provides support (e.g. creates regions of lesser flexibility) and may be any shape (e.g. a cylinder, a sphere, a straight bar, a wavy bar, a serpentine ribbon, etc.). A bar or other joining or support material may be connected with the bioerodable material using any means (e.g. heat or mechanical). The additional joining material may be the same material as the bioerodable portion or may be a different material.

[000108] A bioerodable material that is coupled to itself may be any shape that is able to maintain a shape of the long term implant and/or resist a compressive force (or maintain a tensioned force) from the long term implant. As shown in implant system 200 in FIG. 23 A, B, additional joining material 204 may couple two long sides 202, 203 of C-shaped or cuff shaped material 207 to hold long-term elongate implant 208 in an elongated position. A C-shaped or cuff shaped material may be easy to manufacture and may be easy to place (e.g. snap) over an elongated implant, and the additional joining material may hold the C-shaped material in place (e.g. prevent the cuff from falling off the elongated implant) so that it is able to resist a compressive force from wide section 206 to thereby place or hold long term implant 208 in an elongated shape. Although shown as a continuous material, a C-shaped bioerodable material may

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have any number of holes or open spaces. Holes or open spaces may improve device flexibility prior to bioerosion compared with a solid structure, and/or may allow better penetration of a body fluid. This may allow better timing of device erosion which in turn may influence both device anchoring and device function. In some embodiments, a bioerodable structure may be essentially a cylindrical structure that envelops an axis or envelopes part of an axis of a long term implant portion. A cylindrical structure (e.g. an open ended tube) may be continuous or may include open spaces (e.g. holes, slots). A bioerodable implant described herein, including a cylindrically shaped bioerodable implant, may be made by any means and may be connected with a long term implant using any methods or any means. In some embodiments, a portion of a bioerodable implant may be placed over a long term implant and then fastened in place (e.g. In FIG. 23, joining material 204 in FIGS. 23 A-B may extend along the length of sides 202, 203 to form a cylindrical structure. Alternatively, a bioerodable implant may be manufactured as an extruded tube or may be formed using a mold, and after forming may be placed over the long term implant.

[000109] Any method or structure that allows the bioerodable portion to maintain a long term implant in a desired shape for a desired period of time may be used. A bioerodable material may be coupled to itself using a mechanical joining to hold two (or more) portions of bioerodable material together. Any form of mechanical joining may be used (e.g. forming a crimp, mating complementary portions together).

[000110] In one embodiment, a bioerodable portion may be coupled with one or more other bioerodable portions. Two C-shaped bioerodable pieces, each of which wraps partially around an axis (e.g. a long term implant portion) may be coupled (e.g. bridged) to one another. More than two (e.g. a series) of C-shaped or other shaped bioerodable pieces may be coupled together as shown in FIG. 24 to form system 180 with a modular, mechanically interlocking bioerodable portion around long term implant 208. Each piece may wrap a short distance (e.g. about a quarter of the way), halfway, or more than halfway (e.g. three-quarters of the way to form a C shape or all the way) around an axis, such as an elongate long term implant axis. The pieces may have any conformation and may have features (e.g. snap fit, lock and key,) to lock two or more than two pieces together and/or to lock or otherwise connect a piece with a long term implant portion. In one embodiment, the C-shaped (or other shaped) bioerodable pieces may be lined up (e.g. to substantially form a cuff shape that is open along one side similar to the cuff in FIG. 23 A, B) or bioerodable portions 182, 184, 185 may be offset from one another relative to an elongate axis as shown in FIG. 24. Offset shapes may provide ease of assembly and/or may provide better (overall or local) implant flexibility, due to the presence of an open space, such as space 186 configured to allow implant bending. Having a space, such as space 186, may also minimize an

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amount of biodegradable material present in a device, which may in turn minimize or prevent a side effect (such as inflammation) after a device system has been implanted in a body and the bioerodable portion has bioeroded.

[000111] One aspect of the invention provides a method of manufacturing a bioerodable implant including the steps of wrapping a bioerodable material at least partway around an axis to create a wound bioerodable implant, the bioerodable implant having two points, and coupling the two points to each other. See, for example, FIG. 21. Any biocompatible, bioerodable material can be used, including any described elsewhere in this application or known in the art.

[000112] Another aspect of the invention provides a method of manufacturing an implant system, the implant having an elongate (or resilient) implant body and a bioerodable support material configured to hold the elongate (or resilient) implant body in a first, elongate shape, including the steps of wrapping the bioerodable support material at least partway around the implant body, the bioerodable support material having two points on it, and coupling the two points with each other to create a coupled bioerodable support material.

[000113] In one embodiment, a thin strand of a polymer may be wrapped around an axis to create a helix and the helix may be coupled to itself. In one embodiment, a polymer may be based on lactic acid and/or glycolic (e.g. poly(lactic acid) or poly(DL-lactic-co-glycolic acid)) or any of the materials listed above or known in the art. The method may further include applying an expansive force to the elongate long term implant with the bioerodable material to thereby place or hold the long term implant in an initial shape, as shown in FIG. 21. A coupling step may include attaching (e.g. by applying an adhesive, by applying an other chemical (such as a polymer initiator), or by supplying an energy source) to two points on a bioerodable material to create a support strut. FIG. 21 shows applicator 134 applying an activator (e.g. an adhesive, another chemical or an energy) to thereby fuse two points on the bioerodable material. Coupling the bioerodable may include heating the bioerodable material to melt the two points together. A bioerodable material may additionally (or instead) be coupled with a long term implant portion.

[000114] Another aspect of the invention provides a method of manufacturing an implant system, the implant having an elongate, resilient, long term implant body and a bioerodable (support) material configured to hold the resilient implant body in a first, elongate shape, the method including the steps of wrapping the bioerodable support material at least partway around the implant body (or at least partially enveloping the elongate implant body with a bioerodable support material), the bioerodable support material having two points on it; and coupling the two points with each other to create a coupled bioerodable support material.

[000115] In one embodiment, a ribbon like bioerodable material 172 is wrapped at least partway around axis 174, as shown in FIG. 25. The ribbon may overlap on itself. Two points on

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the ribbon-like material may be coupled to create a first bridge 178 which has less flexibility than other points on the ribbon-like material. The bridge may be created by chemically joining two loops of the ribbon, by adding a new (bioerodable) structure between the two loops, or by mechanically interlocking the loops. Other bridges may be made between other loops of the ribbon-like material. In other embodiments, each loop may be coupled with one (or more than one) other loop(s). An end of the ribbon may abut wide region 176 of the long term implant to thereby place (and/or hold) implant 170 into a first shape. The ribbon-like material may have smooth edges or may have shaped edges. Shaped edges may be configured to couple, or mechanically connect (e.g. interlock). FIG. 26 shows implant 160 with ribbon-like material 162 being wound around long term implant 168. Adjacent sections of ribbon-like material may mate to hold ribbon-like material 162 in place. Any features that are able to hold the ribbon-like material together (and/or prevent it from unwinding relative to the long term implant) can be used. For example, the features may be tongue and groove or lock and key. A ribbon-like material may provide an expansive force to a long term implant portion; for example to wide section 175.

[000116] FIG. 27 shows another embodiment of an implant system with a bioerodable material configured to hold a long term implant in an initial or first shape. The bioerodable material may include a mesh or series of loops (e.g. a stent) that envelop or hold a long term implant to create implant system 210. The loops may wrap all the way around the long term implant or may wrap partially around. Loops 212, 213 may be coupled with each other to create bridge 218 of relatively lesser flexibility relative compared with the rest of the loop(s).

[000117] Alternatively, or additionally to being coupled to itself, the bioerodable material may be coupled with the long term implant. The bioerodable material may be coupled with the long term implant using any method or any material(s). The coupling may serve to hold the bioerodable material in a desired shape or configuration. A bioerodable material and a long term implant may be coupled using any chemical or mechanical means, including any described elsewhere in this application. As shown in FIG. 27, they may be coupled using corresponding mating structures 214, 222.

[000118] The bioerodable material may have regions of different flexibility. The regions may hold or help hold the bioerodable material (and the long-term elongate implant) in a preferred shape. FIGS. 28 and 29 show implants with bioerodable material having regions of differing flexibility. FIG. 28 shows implant system 230 with a bioerodable spring coiled around a long term implant. The coils of the spring have regions 234, 236 that are less flexible than other portions (the rest) of the coils of bioerodable portion 232. For example, these regions may be thicker, wider, or may include a different material with different resiliency (e.g. different

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flexibility). Any number of regions of lesser flexibility may be present on a coil. For example, each coil may have a second region of lesser flexibility on the coil (e.g. half-way around the coil) such that each coil has two regions of lesser flexibility (hinges) that control (e.g. prevents or reduces) a rotation or other movement of the coil. Figure 29 shows implant 240, which is similar to the device shown in FIG. 28, but regions of lesser flexibility 244, 246 in bioerodable portion 242 are staggered relative to one another. Staggering a region having a lesser flexibility relative to another region of lesser flexibility may prevent the coil from unwinding while simultaneously allowing the coil (spring) to bend in various directions and to accommodate motion of the airway tissue (e.g. physiological movements, such as eating, breathing, or speaking).

[000119] The bioerodable material may have one or more than one (a plurality) of coils that wrap around a long axis (e.g. around a long-term elongate implant axis) no times (e.g. be a straight bar or a curve bar), or may wrap around the axis up to 1 time, up to 2 times, up to 3 times, up to 4 times, up to 5 times, up to 10 times, up to 20 times, up to 30 times, up to 40 times, or more than 40 times. FIG. 30 shows an embodiment of implant 250 in which bioerodable material 252 winds around (at least partially envelopes) the long term implant one and a half times. The bioerodable material may partially envelop the long term implant portion (as shown in FIG. 30) or may almost completely or may completely envelop the long term implant portion. The bioerodable material may be coupled with a long term implant at wide region 254 to create a region of lesser flexibility on the bioerodable material.

[000120] The long term implant portion may have none, one or more than one wide portions that separate narrow portions. The wide portion may have a tensioned configuration and may provide a compressive force to the bioerodable portion such that the bioerodable portion holds the long-term implant portion in a preferred shape. FIG. 31 shows implant 260 with two wide portions and a single spring 262. The single spring (helix) partially envelops a narrow portion and is coupled with itself at two points at bridge 268 near an end of the helix and at bridge 266 near a central portion of the helix. In addition, or instead, the spring may be coupled at the other end of the helix (coil), and/or may be coupled at one or more places along the middle portions of the spring. The bioerodable portion may be coupled with the long term implant though bridge 264 to hold the long-term implant portion in a preferred shape. The bioerodable portion may be coupled with the long-term implant portion is any way.

[000121] The long-term implant portion may couple with the bioerodable portion in any way (e.g. chemically, mechanically). FIG. 32 shows implant system 270 in which wide portion 274 of the long term, resilient, elongate implant includes channel 276 configured to accept a cross portion 278 of bioerodable material. A channel may grip or hold a cross portion of bioerodable material or the channel may provide a passage for a cross portion without gripping it. A cross

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portion may be configured along with section 272 of a bioerodable helix to resist a compressive force or provide an expansive force to a long term implant portion, including to channel 276. In one method of manufacturing an implant system with an implant having a resilient (or elongate) implant body including an implant body point and a bioerodable support material configured to hold the resilient (elongate) implant body, the method includes: wrapping the bioerodable support material at least partway around the implant body; and coupling the bioerodable support material with the implant body. The bioerodable support material may be coupled with the implant body using any means (e.g. chemical or mechanical). In one example, the first portion is a narrow portion and the second portion is a channel in a wide portion, the channel configured to hold the bioerodable material, and the bioerodable support material is passed through or along a surface of the channel. The implant body (channel) may hold the bioerodable material or the bioerodable material and the implant body may be fastened together, such as by a lock and key or a chemical coupling.

[000122] If different and multiple regions of coils are fused, a range of contraction times of the long term implant portion could be generated. Note that coil diameter also contributes to rate of contraction but may be secondary to coil fusion. In in vitro tests, the durometer of the material influenced contraction in the least significant manner. Nonetheless, taken together these parameters could be used to generate a matrix of physical properties that could influence the timing of the degradation of the coils, as well as match the bending properties of the device as a whole to tongue or other airway implant motion.

[000123] Any of the features described herein may be combined with any other features herein or as is known in the art. For example, any implant or any system may have a region(s) configured to be externally identifiable or visible or made externally identifiable or visible (e.g. by fluoroscopy), such as to a health care provider (physician) to aid in device placement, device tracking, and/or device removal. A region, such as wide sections 108 shown in FIG. 19 A-D for example or at least part of anchor end 104 may be platinum or other identifiable material. An implant or system may have a plurality of regions that are identifiable. In another example, any of the devices may be configured to be easily removable. FIGS. 33 and 34 illustrate another embodiment of revisable OSA implant 300 that includes at least one end with an encircling portion indicated at 315 that encircles or surrounds a tissue plug 316 that grows through an opening 320. In one embodiment, the implant carries a cut wire 322 that extends in a loop with first and second wire ends 324A and 324B extending through one or more passageways in the implant. The cut wire 322 can be embedded in the surface of the implant surrounding the opening 320. As can be seen in FIG. 34, the looped cut wire 322 can be pulled proximally to cut the tissue plug 316 which then will free the implant from its attachment. In FIG. 33, it can be

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seen that the cut wire ends 324A and 324B can have a serpentine configuration in the medial portion of the implant so as to not interfere with the tensioning and relaxation of the elastomeric medial implant portion during its use. When the cut wire is accessed and pulled relative to the implant 300, the tissue plug 316 can be cut. It should be appreciated that other tools (not shown) may be used to stabilize the implant when actuating the cut wire as in FIG. 34. The cut wire 322 can be any form of fine wire, or abrasive wire or a resistively heated wire coupled to an electrical source (not shown).

[000124] FIG. 35 depicts another revisable OSA implant 300' that is similar to that of FIGS. 33-34 with the cut wire 322' configured to cut a plurality of tissue plugs 316 that have grown through openings 320 within an encircling end portion of the implant body.

[000125] The devices may alternatively, or additionally, have reinforced anchor portions. The reinforced anchor portions may allow tissue to grow on or through an anchor portion and may serve to better anchor a device in place. The reinforced anchor portions may help hold an implant in place and/or may keep an implant from undergoing undesired stretching.

[000126] FIGS. 36A and 36B further illustrate that the anchor portion's axial length of AL (or AL') can have a selected relationship to the medial portion's axial length ML (or ML'), and thus the overall implant length which is dependent on the desired amount of axial retraction forces applied by the implant. For example, in FIG. 36A, in one embodiment each anchoring end length AL can be 15% of the overall length of the implant which has a medial portion 1115 configured to apply a retraction force of 3.0 Newtons. FIG. 36B depicts another embodiment wherein each anchoring end length AL' can be 35% of the overall length of the implant and the medial portion 1115 with length ML' can still be configured to apply a retraction force of 3.0 Newtons. In this embodiment, the design in FIG. 36B may be preferred because of the increased anchoring length, which would decrease the likelihood of tissue remodeling over time.

[000127] Referring to FIG. 37, it can be seen that an anchoring end portion 1010a of an OSA implant is made axially inelastic by means of non-stretchable reinforcing filaments or elements 1022 embedded therein. Such filaments 1022 can be an inelastic, flexible polymer (e.g., Kevlar®, or polyester), metal wires (e.g. stainless steel, NiTi), carbon fiber or the like. The filaments 1022 can be substantially linear elements or can be knit, woven, non woven, or braided structures as in known in the art. In another embodiment, the anchoring end portion may be made of a non-stretchable material without the addition of reinforcing filaments or elements. As can be understood from FIG. 37, the end portion 1010a is thus axially inelastic but is still flexible and twistable relative to axis 1008.

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[000128] The devices described herein may be combined with other device features, including, but not limited to those described in U.S. 8,167,787, U.S. 2011/0144421, U.S. 2011/0226262, and U.S. Patent Application No. 13/308,449 to Gillis et al. filed November 30, 2011.

[000129] Any of the devices or systems described herein may be configured to substantially hold the bioerodable material and/or may be configured to hold the long term implant in an initial (e.g. a first or a non-final) shape or configuration for less than 16 weeks (e.g. between 2 and 6 weeks, between 3 and 5 weeks, or for less than 1 week, less than 2 weeks, less than 3 weeks, less than 4 weeks, less than 5 weeks, less than 6 weeks, less than 7 weeks, or less than 8 weeks) when exposed to a body fluid or a saline solution. A body fluid that the device may be exposed to may be, for example, blood, interstitial fluid, lymph, mucus, nasal exudate or discharge, and/or saliva. A saline solution may be any saline solution, including a buffered saline solution. In one particular example, it is 0.1 M saline (0.1 M sodium chloride). After exposure to a body fluid for a sufficient period of time, an implant may take on a second, final, or therapeutic shape or configuration.

EXAMPLES

[000130] EXAMPLE 1. Implant contraction accelerated testing

[000131] An in vitro test system was developed to demonstrate the fatigue behavior of the restricting coils and simulate the expected motion after implantation. While not wishing to be limited to any theory, it is thought that the characteristic motions of the coiled implant when implanted are initially multiplanar bending. While some stretching of the device may occur, contraction is substantially prevented until the supporting coils degrade.

[000132] In order to evaluate the relative performance of types of coils, sets of implants with different durometer silicone cores and with coils that were either fused or open-ended within segments were rested. Coils with diameters of 0.009" or 0.013" were tested in 0.1M saline at 37°C in a 20 L bath. The coils were made to oscillate by fixing one end and placing the body of the implant in a moving stream such that bending occurred at an approximate frequency of 2Hz with a randomly oriented 15 degree to 30 degree bending motion. Bacterial growth was inhibited by addition of 0.01% sodium azide. Solutions were replaced each week and refreshed daily to replace fluid lost by evaporation. Temperature was maintained with the use of a submersible thermocouple regulated coil heater.

[000133] In general, regardless of the durometer of the silicone core tested, coil segments that were not fused at both ends began to unravel at their distal ends, causing a decrease in the stretched length of the implant from 36+/-1 mm to 21 to 27 mm by day 10 of the test. In

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contrast, implant systems with coils that were fused relaxed a stretched length of about 36 mm to about 34 mm by day 10.

[000134] Silicone cores with unfused coils contracted to 18 mm, which is their relaxed state, by day 15. For the fused coil materials tested, the rate of contraction depended little upon the durometer of the material or the diameter of the coil. The higher durometer (50 D) material tested with 0.013" diameter fused coils contracted the least, contracting to only about 34 mm. 40 D material tested under the same conditions contracted to about 32 mm. This difference is small compared to the contraction levels observed in unfused coils and shows that although use of a higher durometer material can greatly increase the force on the coils, its effect is far less significant than is coil fusion. This suggests that the greatest impact on maintaining stretched implant length and avoiding early (premature) contraction was created by fusing coils.

[000135] EXAMPLE 2. The effect of fusing implant coils together to prevent the coils from prematurely unwinding on the implant contraction rate was further tested using a canine animal model. Comparable implant systems having resilient, long term implants initially held in expanded shapes by coiled bioerodable implant material with (FIGS. 38 C-D) and without (FIGS. 38 A-B) fused coils were placed on both left and right sides of animals' tongues and soft palates and the bioerodable material bioeroded to allow the resilient, long term implants to foreshorten. The implant lengths were measured as a function of length of time since implantation. Noting that the time scales are different, as seen by the more gradually downward sloping curves going from the initial implant lengths (at time=0) to the equilibrium (foreshortened) implant lengths in the results shown with the fused coils placed in the right and left sides of the tongue ("Right tongue" and "Left tongue", respectively) as shown FIGS. 38 C-D compared with the steeper, downwardly sloping lines obtained from the corresponding unfused implants shown in FIGS. 38 A-B, resilient implants with fused bioerodable coils placed in the tongue shortened more slowly and took a longer overall time to reach a (fully) foreshortened length than did resilient without fused bioerordable coils. Systems with fused coils took several weeks (e.g. more than 22 days and possibly as long as 25-40 days or more) to contract to about 20 mm, about the same implant length that systems having unfused coils reached by about 10-14 days after implantation. Comparing results of fused coil implant systems (with unfused coil implant systems in the tongue (FIGS. 38 A-D), bioerodable coil fusion eliminated about 80% of the amount of contraction (foreshortening) observed in the unfused coil system at 14 days. The rate of foreshortening was also slower in implant systems in the soft palate having fused coils compared with implant systems without fused coils (compare results for "Right palate" and "Left palate" in FIGS. 38 A-D).

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[000136] As for additional details pertinent to the present invention, materials and manufacturing techniques may be employed as within the level of those with skill in the relevant art. The same may hold true with respect to method-based aspects of the invention in terms of additional acts commonly or logically employed. Also, it is contemplated that any optional feature of the inventive variations described may be set forth and claimed independently, or in combination with any one or more of the features described herein. Likewise, reference to a singular item, includes the possibility that there are plural of the same items present. More specifically, as used herein and in the appended claims, the singular forms "a," "and," "said," and "the" include plural referents unless the context clearly dictates otherwise. It is further noted that the claims may be drafted to exclude any optional element. As such, this statement is intended to serve as antecedent basis for use of such exclusive terminology as "solely," "only" and the like in connection with the recitation of claim elements, or use of a "negative" limitation. Unless defined otherwise herein, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. The breadth of the present invention is not to be limited by the subject specification, but rather only by the plain meaning of the claim terms employed.

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CLAIMS

What is claimed is:

1. An implant system for treating a sleep disorder comprising a bioerodable material and an elongate long term implant, wherein the bioerodable material at least partially envelops the elongate long term implant and resists a compressive force of the long term implant, the bioerodable material comprising a first region having a first flexibility and a second region having a second flexibility that is less than the first flexibility.

2. The implant system of claim 1 further comprising a plurality of first regions having the first flexibility and a plurality of second regions having the second, lesser flexibility.

3. The implant system of claim 2 wherein the second regions of lesser flexibility are configured to maintain the bioerodable material in an enveloping configuration relative to the elongate long term implant.

4. The implant system of claim 2 wherein the regions of lesser flexibility are configured to substantially hold the bioerodable material in an initial shape for a period of time that is less than 16 weeks upon exposure to a body fluid.

5. The implant system of claim 2 wherein the regions of lesser flexibility are configured to substantially hold the bioerodable material in an initial shape for a period of time between 2 and 6 weeks upon exposure to a body fluid.

6. The implant system of claim 2 wherein the regions of lesser flexibility are configured to substantially hold the bioerodable material in an initial shape for a period of time between 3 and 5 weeks upon exposure to a body fluid.

7. The implant system of claim 2 wherein the bioerodable material comprises a spring having a plurality of coils and the first regions having the first flexibility comprise two coils of the spring.

8. The implant system of claim 7 wherein the second regions having the second, lesser flexibility comprise two points on the coils that are linked with each other.

9. The implant system of claim 1 wherein the elongate long term implant comprises a silicone material.

10. The implant system of claim 1 wherein the bioerodable material comprises a polymer based on lactic acid.

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11. The implant system of claim 10 wherein the bioerodable material comprises poly(lactic acid) or poly(DL-lactic-co-glycolic acid).

12. An implant system for implanting in airway forming tissue comprising a bioerodable material and an elongate long term implant, wherein the bioerodable material at least partially envelops the elongate long term implant and is linked between a first set of two points on the bioerodable material to form a first bridge.

13. The implant system of claim 12 wherein the bioerodable material is configured to hold the elongate long term implant in an initial shape.

14. The implant system of claim 12 wherein the bioerodable material maintains the elongate long term implant in a tensioned initial shape.

15. The implant system of claim 12 wherein the bioerodable material comprises a spring having at least two coils and a plurality of points, and the first bridge connects two points on the spring.

16. The implant system of claim 15 wherein the two points are on different coils at a first end of the spring.

17. The implant system of claim 15 wherein the bioerodable material is linked between a second set of two points on a second set of coils of the spring to form a second bridge.

18. The implant system of claim 17 wherein the second set of coils is at a second end of the spring.

19. The implant system of claim 18 wherein the first and second bridges are bioerodable.

20. The implant system of claim 18 wherein substantially each coil is linked to at least one other coil to form a plurality of bridges.

21. An implant system for treating an airway disorder, comprising:

a resilient elongate implant body having a first insertion shape and a second therapeutic shape; and a

a bioerodable material comprising two coils that at least partially envelop the resilient elongate implant body, wherein the coils are coupled together to form a coupled coil structure.

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22. The implant system of claim 21 wherein the bioerodable material is configured to hold the implant body in the initial insertion shape.

23. The implant system of claim 22 wherein the bioerodable material comprises additional coils continuous with the two coils to thereby form a spring wherein the additional coils of the spring are wrapped around the implant body and the two coils are at an end of the spring.

24. The implant system of claim 23 wherein substantially each coil is coupled to at least one other coil.

25. A method of manufacturing an implant system, the implant having an elongate implant body and a bioerodable support material configured to hold the elongate implant body in a first, elongate shape, the method comprising the steps of:

wrapping the bioerodable support material at least partway around the implant body, the bioerodable support material having two points on it; and

coupling the two points with each other to create a coupled bioerodable support material.

26. A method of manufacturing a bioerodable implant comprising the steps of:

wrapping a bioerodable material at least partway around an axis to create a wound bioerodable implant, the bioerodable material comprising two points; and

coupling the two points to each other.

27. The method of claim 26 wherein the wound bioerodable implant comprises a helix and the coupling comprises heating the helix to thereby fuse the two points.

28. The method of claim 26 wherein the axis comprises an elongate long term implant, and the wrapping around an axis comprises wrapping the bioerodable material around the elongate long term implant to create an implant system.

29. The method of claim 28 further comprising applying an expansive force to the elongate long term implant with the bioerodable material to thereby hold the long term implant in an initial shape.

30. The method of claim 26 wherein coupling comprises attaching a bioerodable material to the two points to create a support strut.

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31. The method of claim 26 wherein coupling comprises applying at least one of an adhesive, an other chemical, or an energy source to the bioerodable material.

32. The method of claim 26 wherein coupling comprises heating the bioerodable material to thereby melt the two points together.

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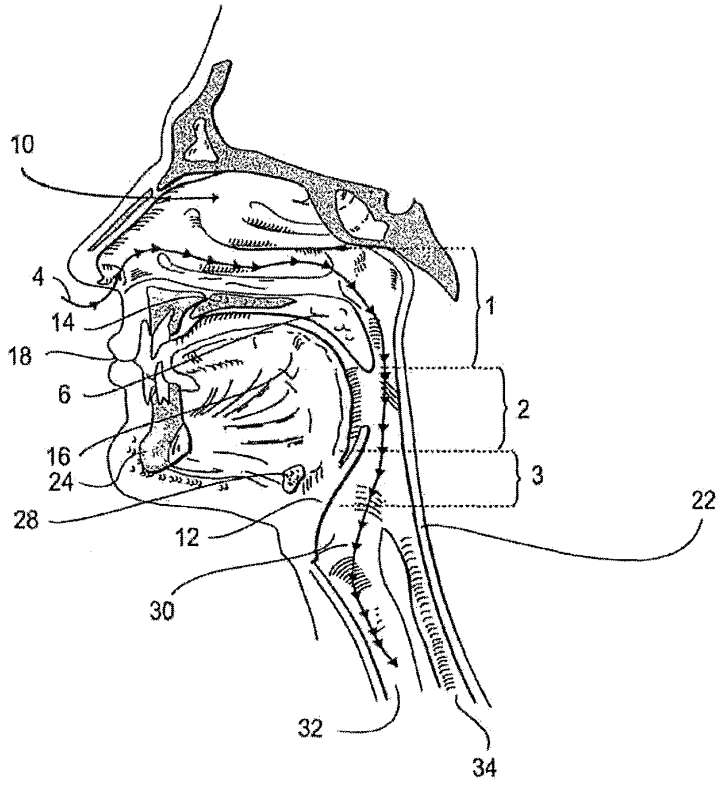


FIG. 1

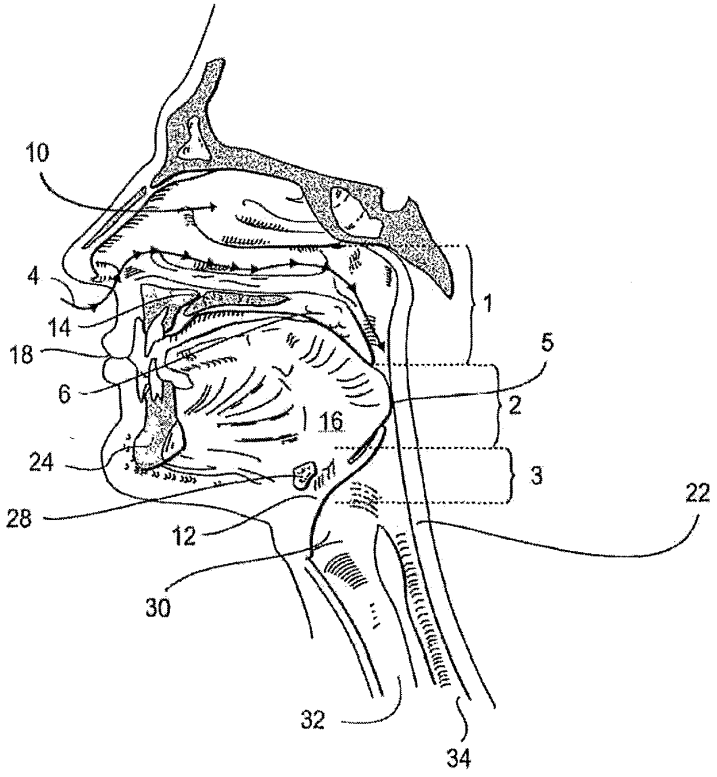


FIG. 2

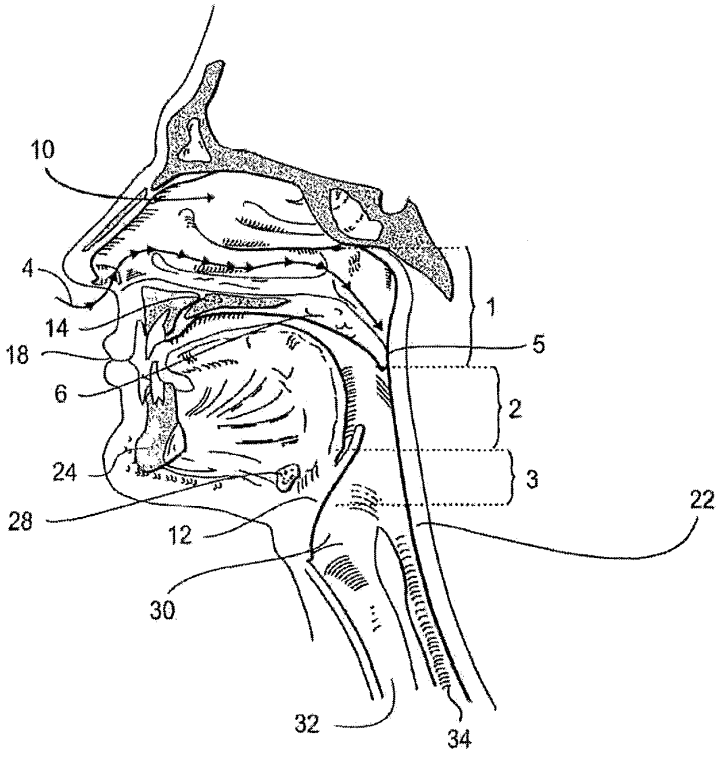


FIG. 3

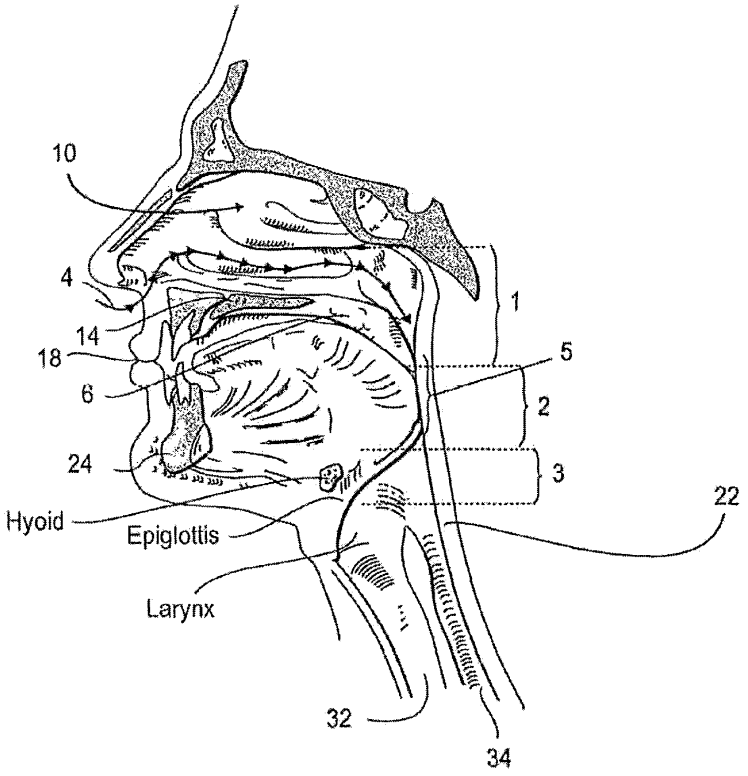


FIG. 4

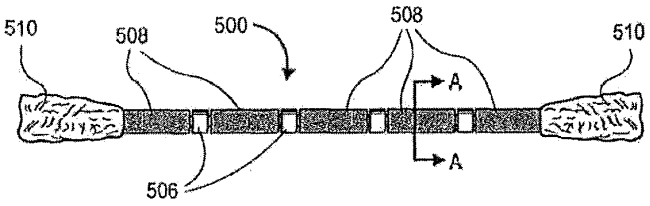


FIG. 5A

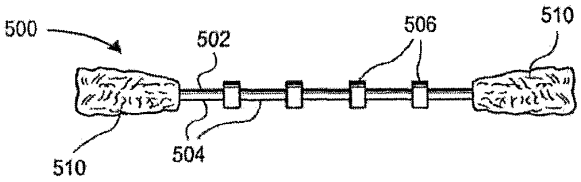


FIG. 5B

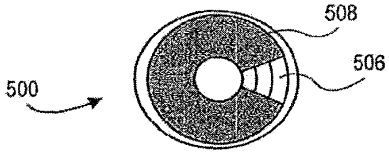


FIG. 5C

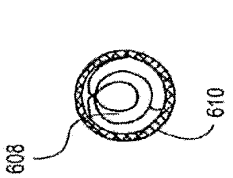


FIG. 6B

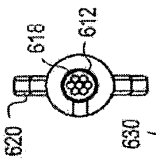


FIG. 6D

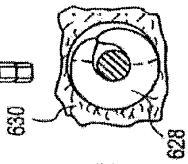


FIG. 6F

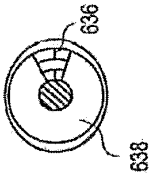


FIG. 6H

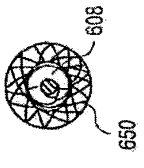


FIG. 6J

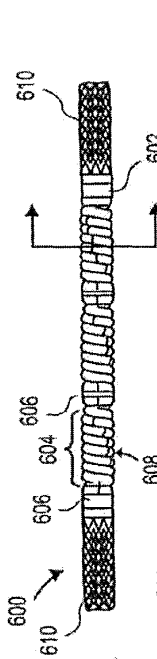


FIG. 6A

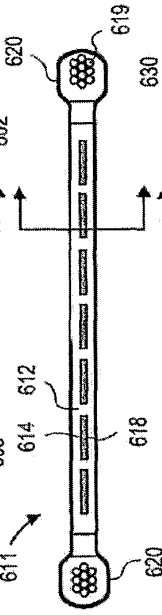


FIG. 6C



FIG. 6E

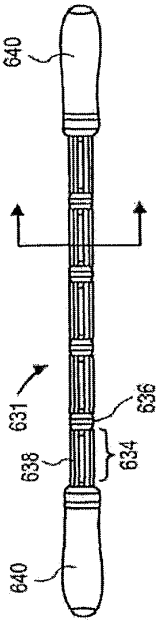


FIG. 6G

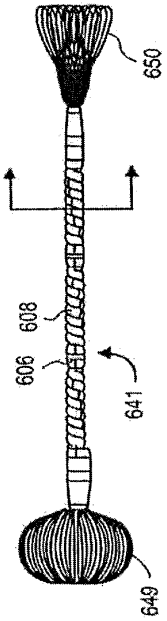


FIG. 6I

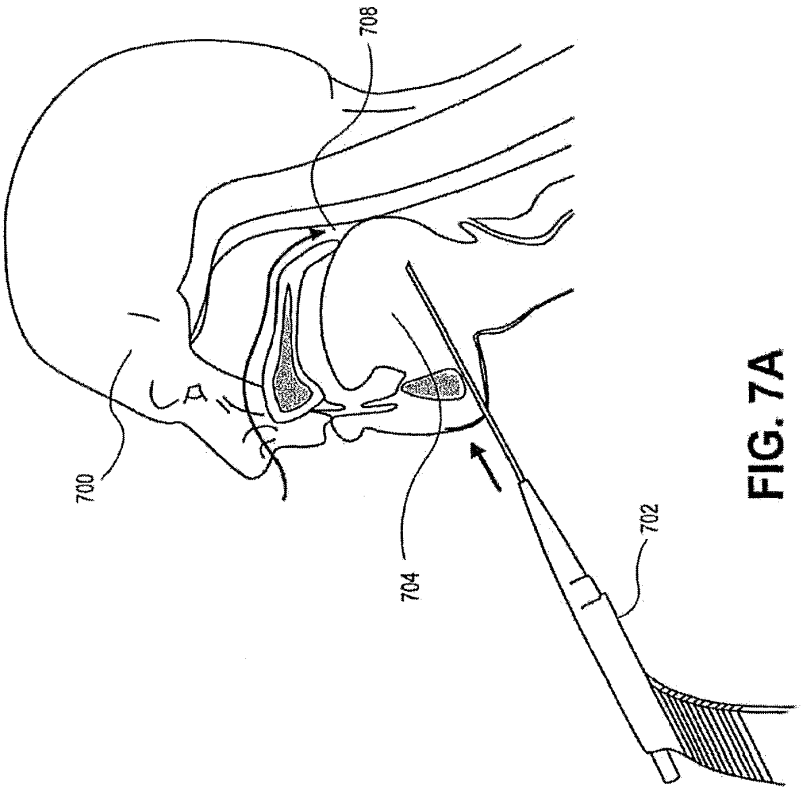


FIG. 7A

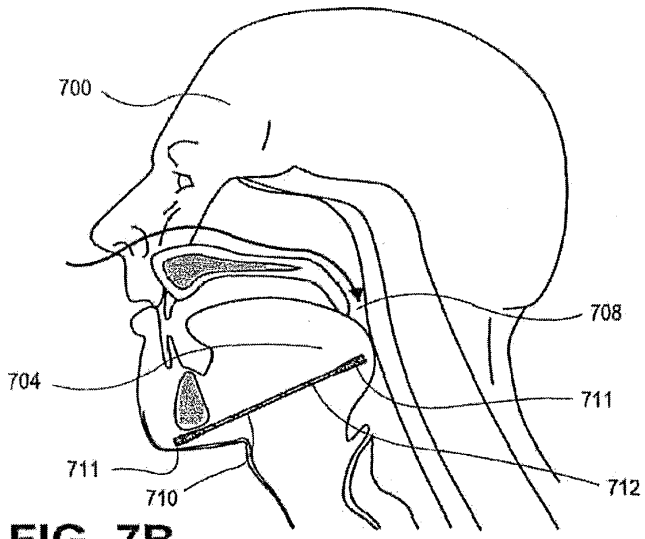


FIG. 7B

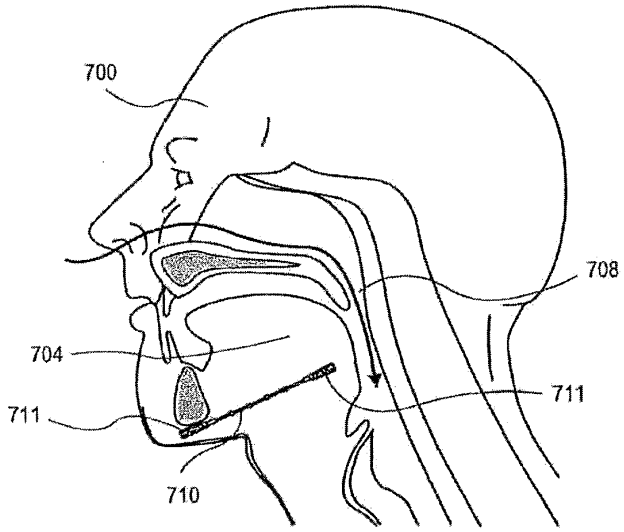


FIG. 7C

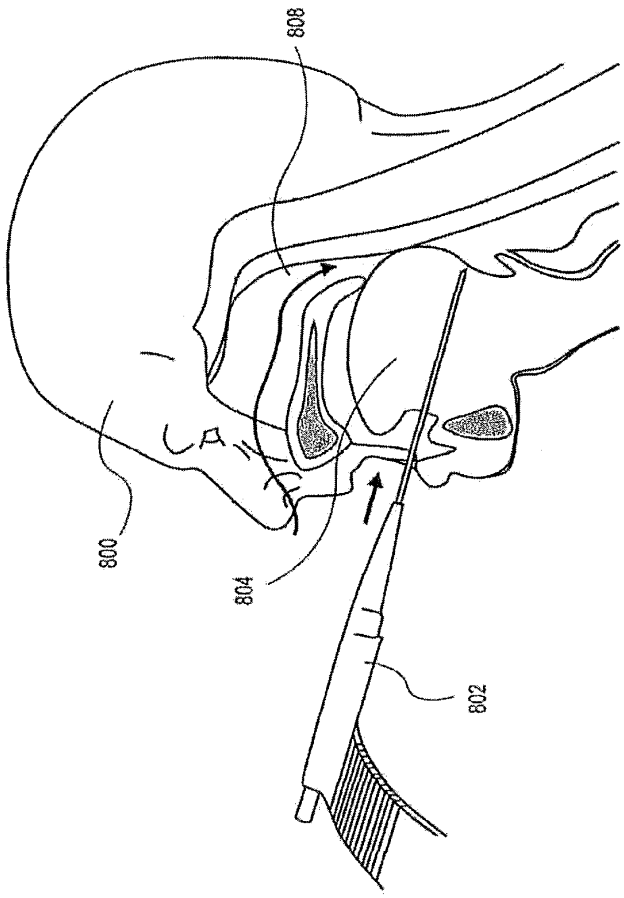


FIG. 8A

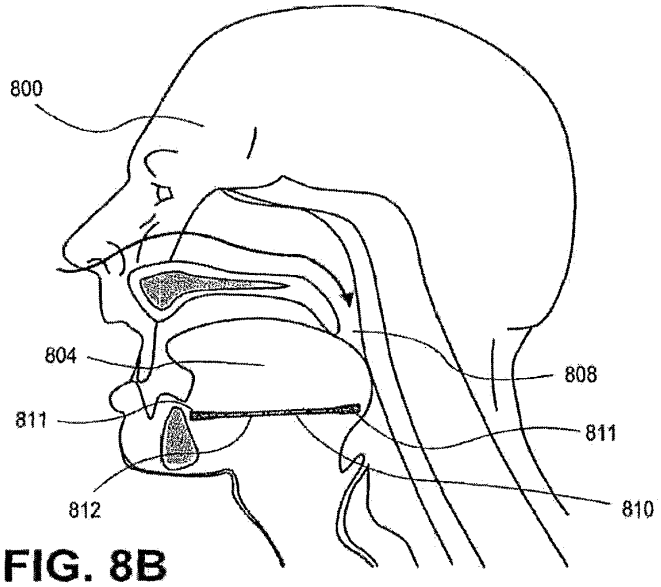


FIG. 8B

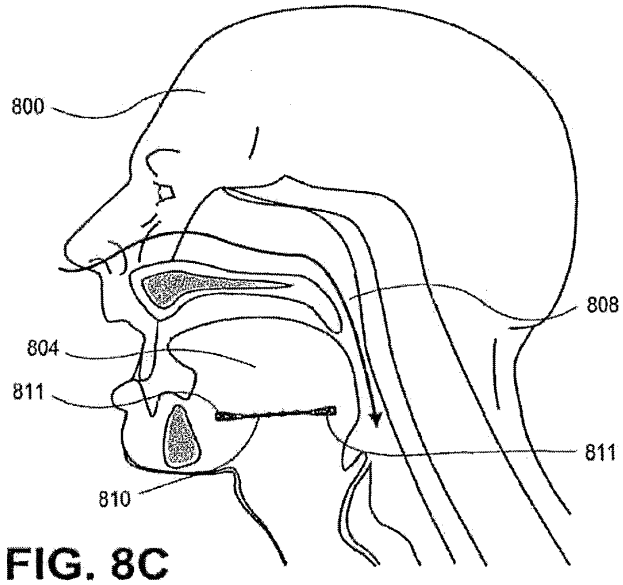


FIG. 8C

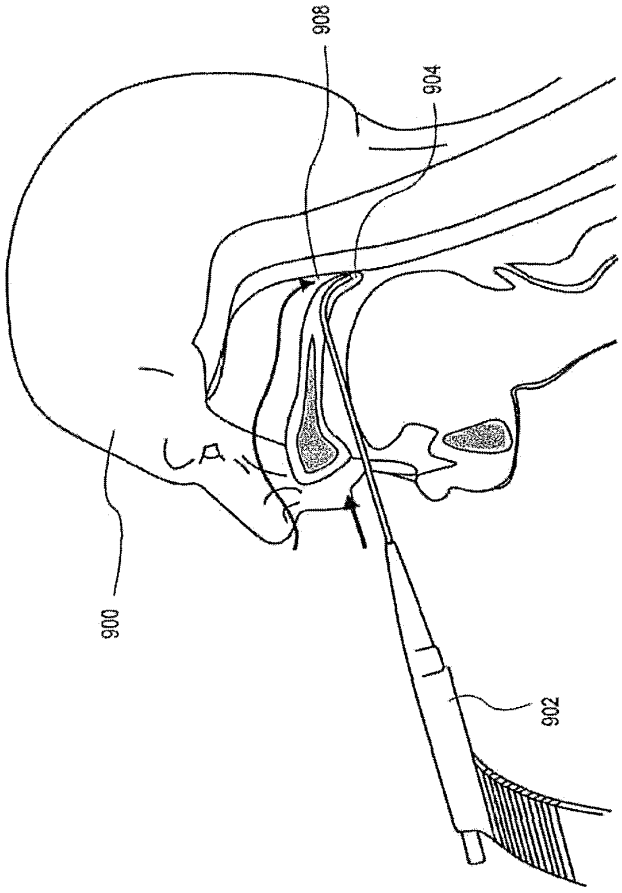


FIG. 9A

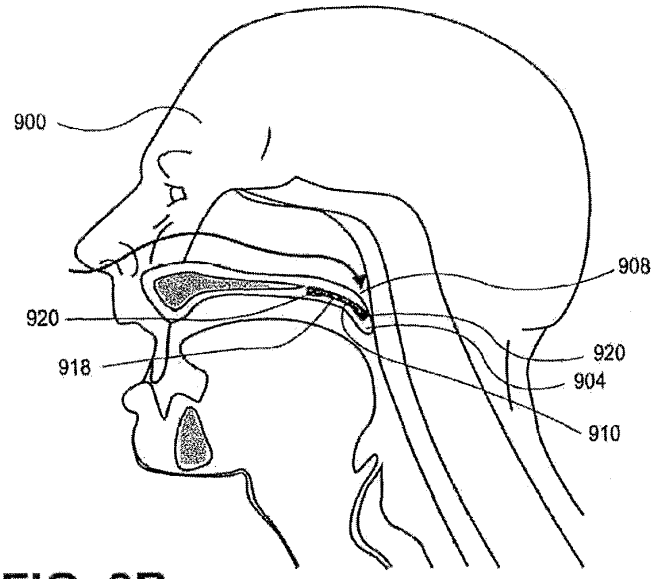


FIG. 9B

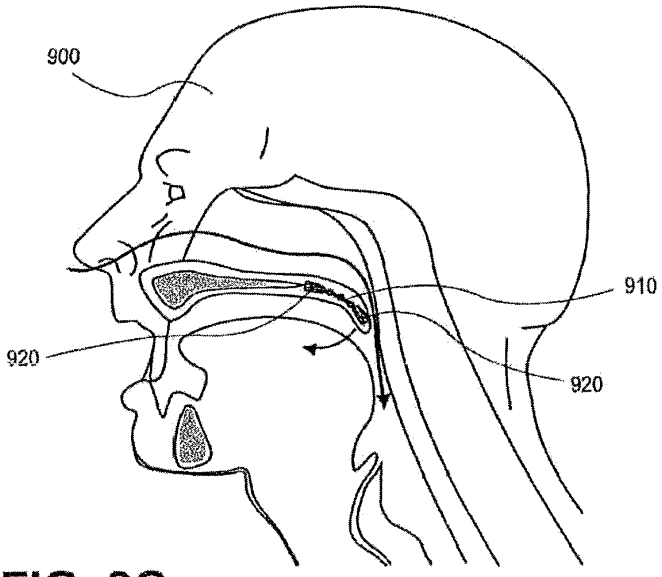


FIG. 9C

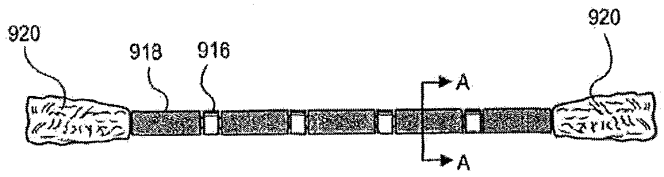


FIG. 10A

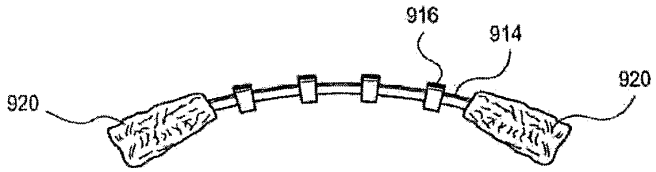


FIG. 10B

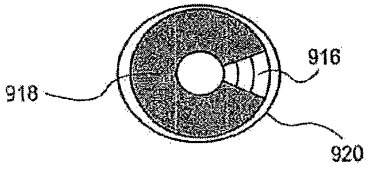


FIG. 10C

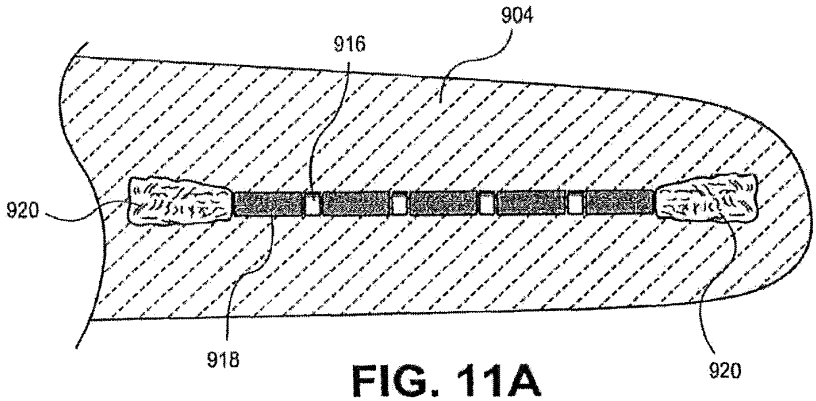


FIG. 11A

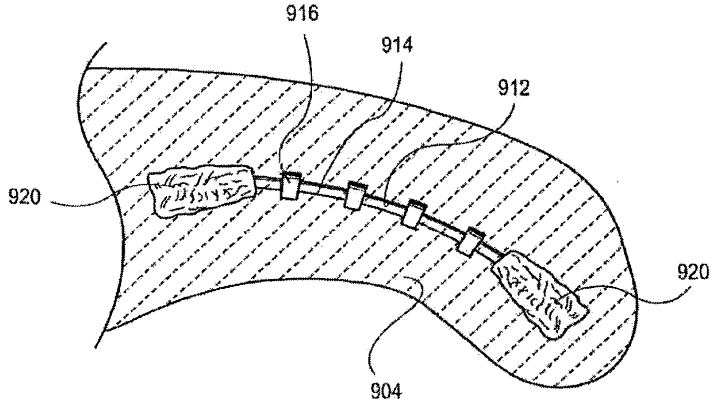


FIG. 11B

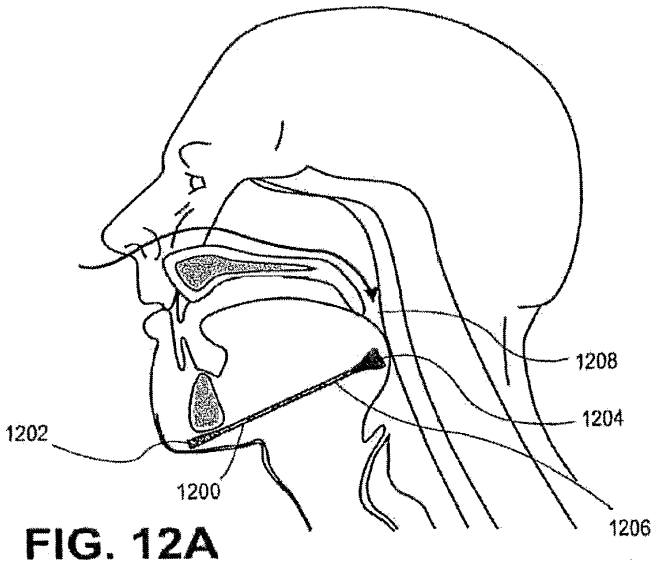


FIG. 12A

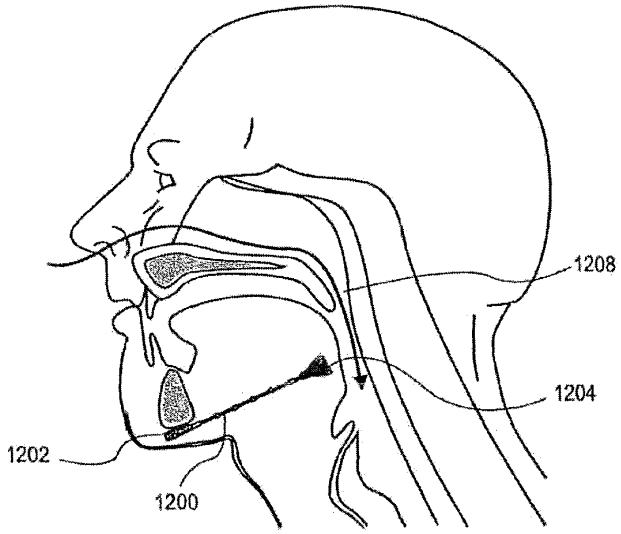


FIG. 12B

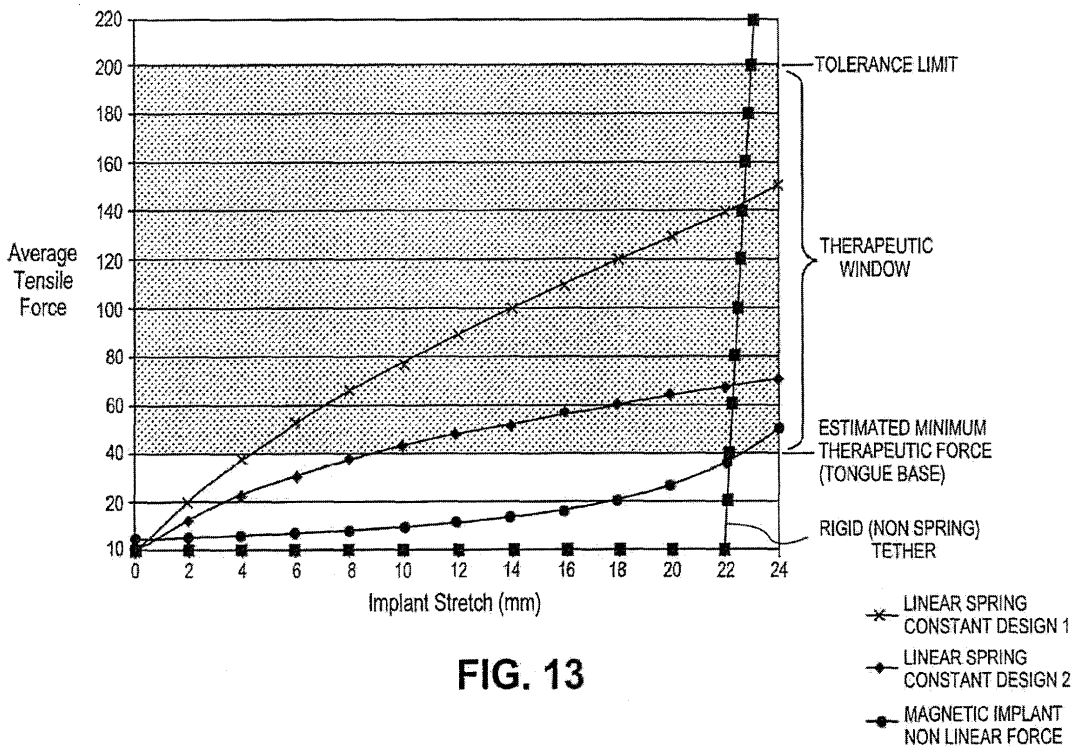

220
200
180
160
140
120
100
80
60
40
20
10
Average Tensile Force
0
2
4
6
8
10
12
14
16
18
20
22
24
Implant Stretch (mm)
TOLERANCE LIMIT
THERAPEUTIC WINDOW
ESTIMATED MINIMUM THERAPEUTIC FORCE (TONGUE BASE)
RIGID (NON SPRING) TETHER
LINEAR SPRING CONSTANT DESIGN 1
LINEAR SPRING CONSTANT DESIGN 2
MAGNETIC IMPLANT NON LINEAR FORCE

FIG. 13

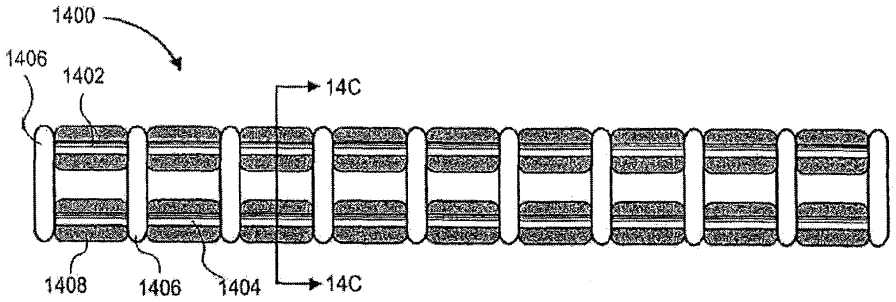


FIG. 14A

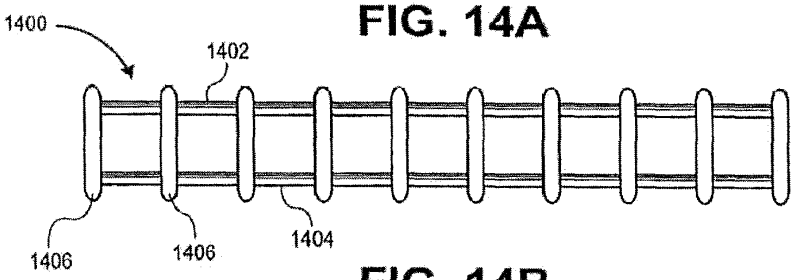


FIG. 14B

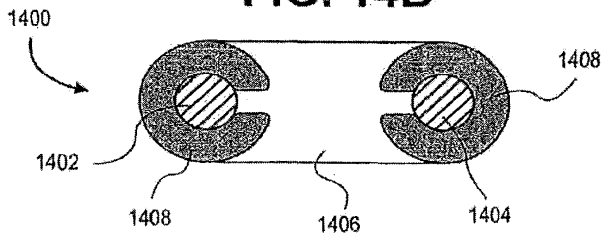


FIG. 14C

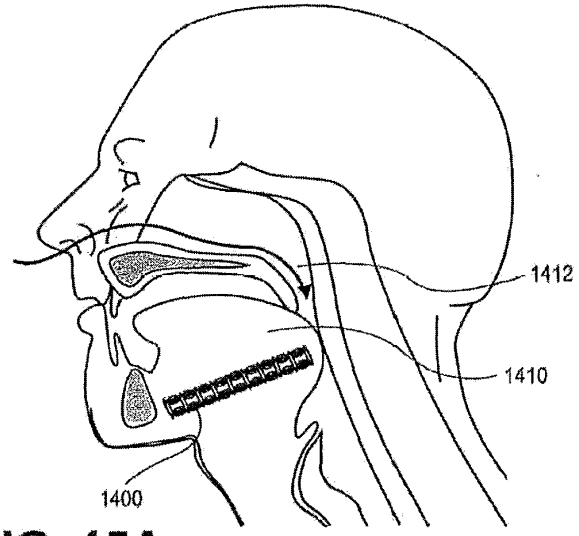


FIG. 15A

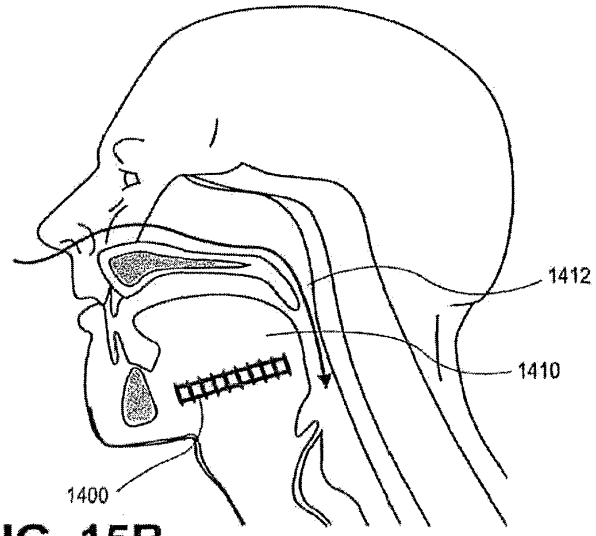


FIG. 15B

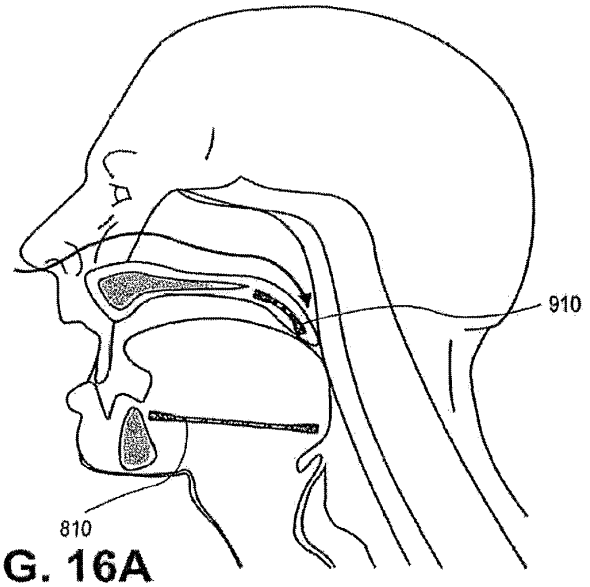


FIG. 16A

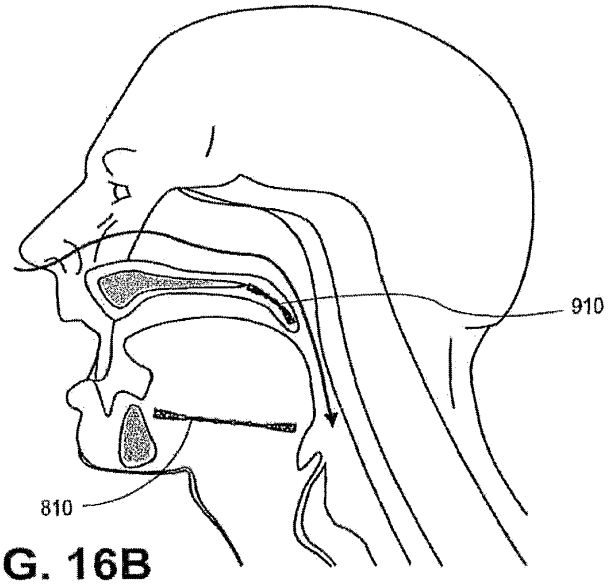


FIG. 16B

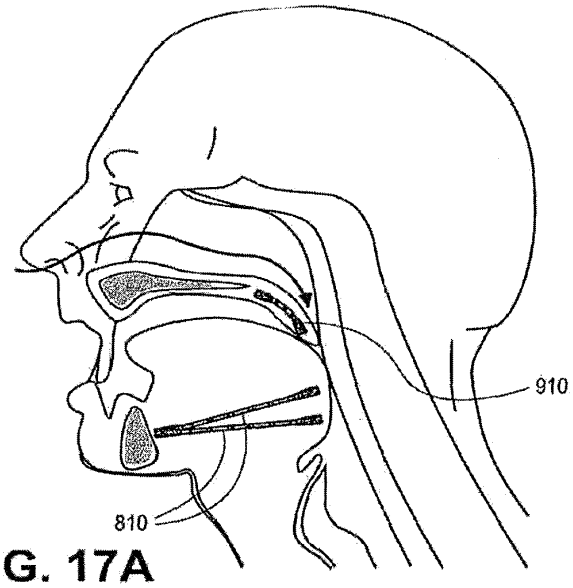


FIG. 17A

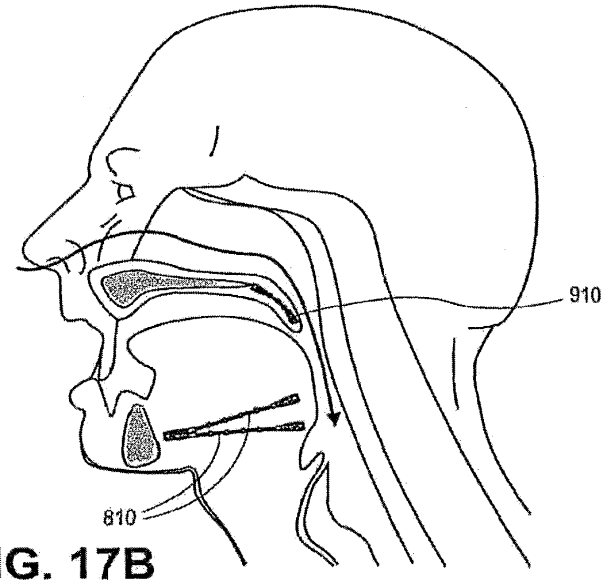


FIG. 17B

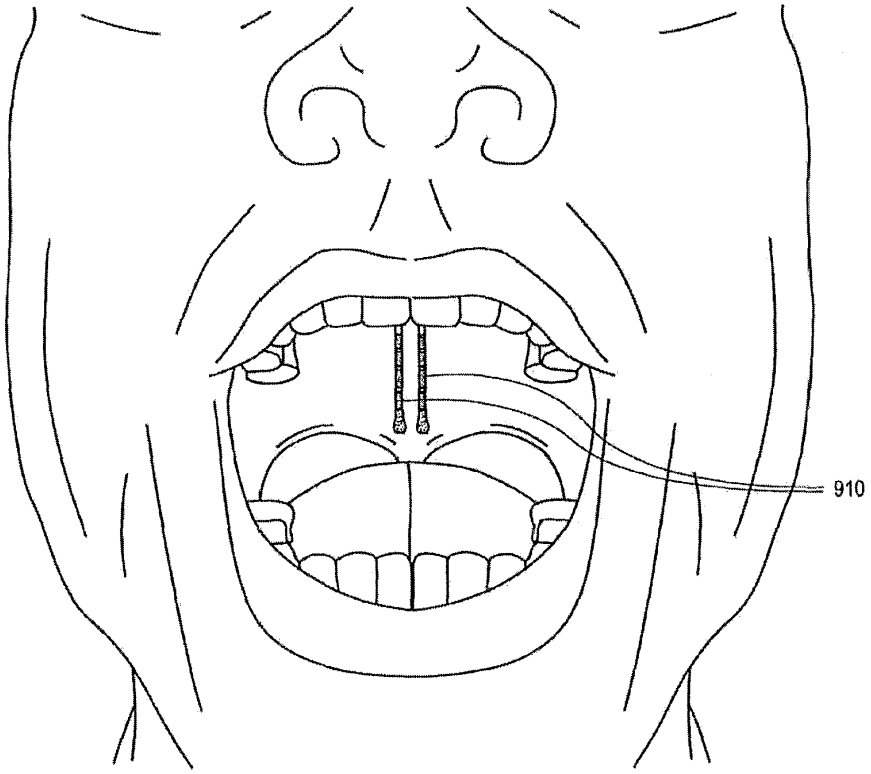


FIG. 17C

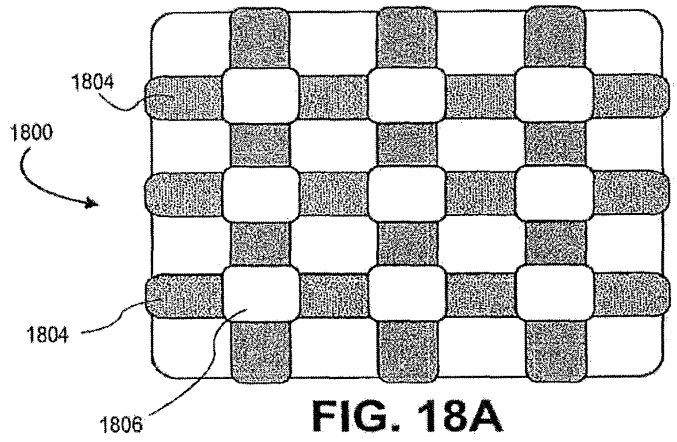


FIG. 18A

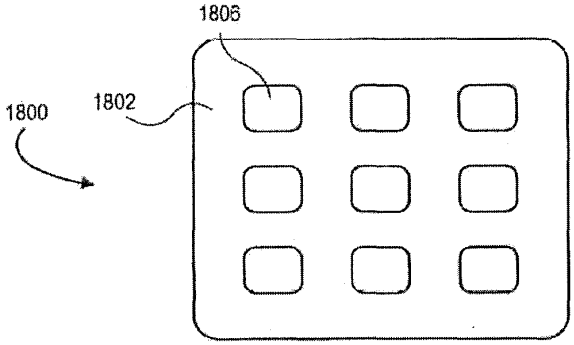


FIG. 18B

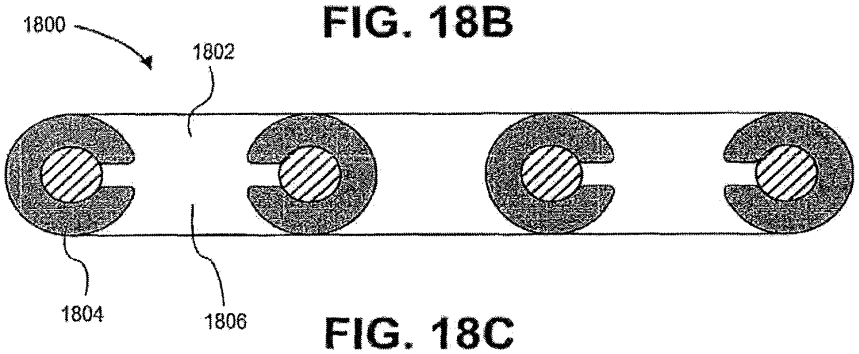


FIG. 18C

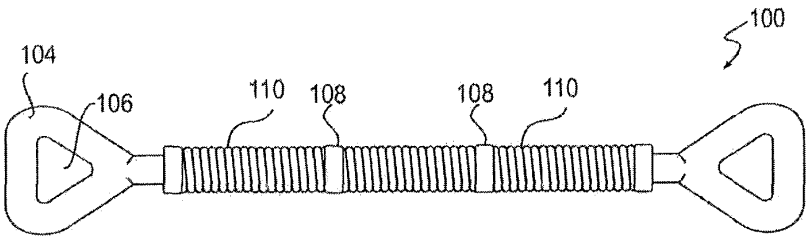


FIG. 19A

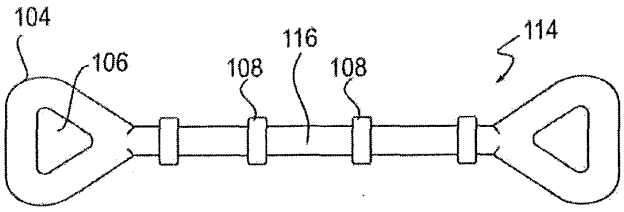


FIG. 19C

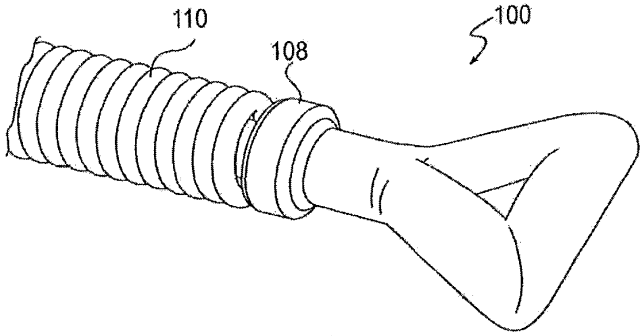


FIG. 19B

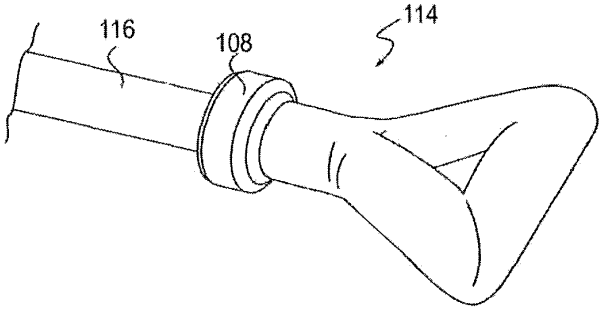


FIG. 19D

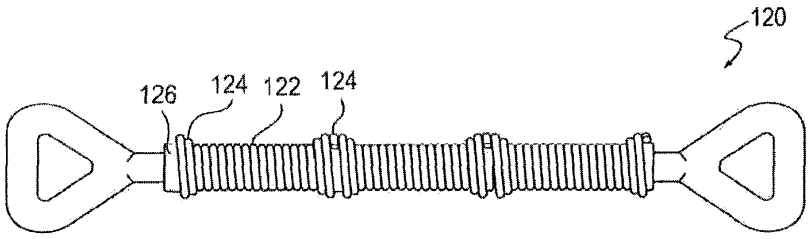


FIG. 20A

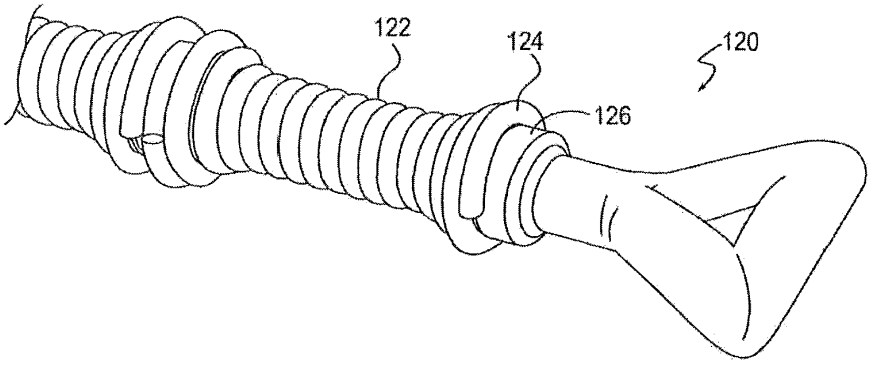


FIG. 20B

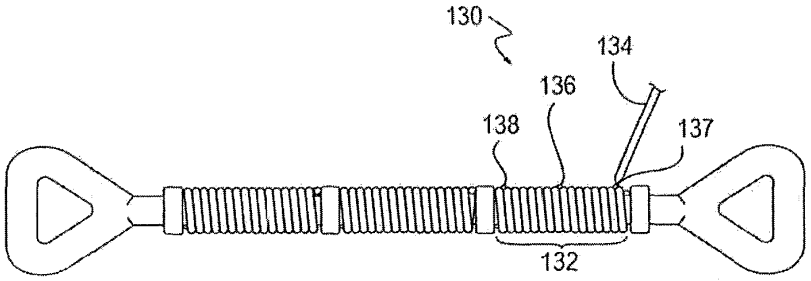


FIG. 21

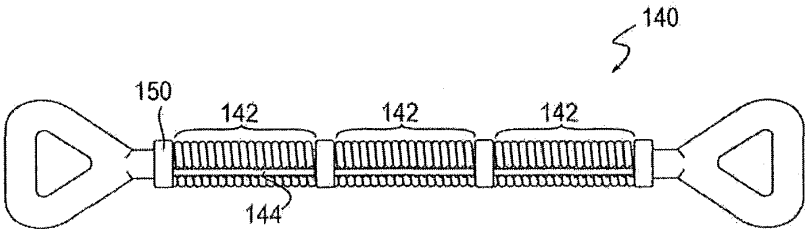


FIG. 22A

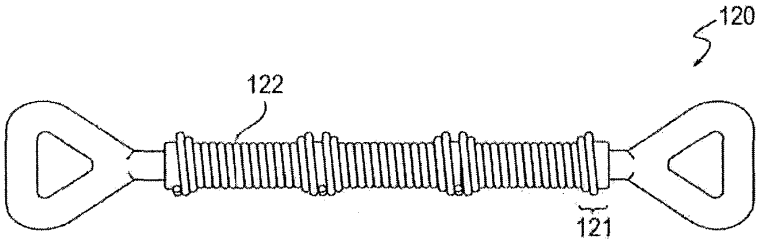


FIG. 22B

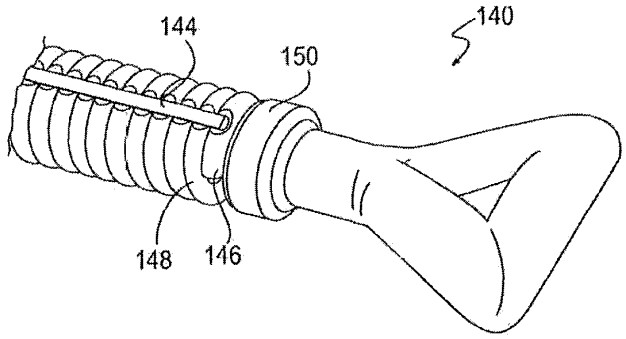


FIG. 22C

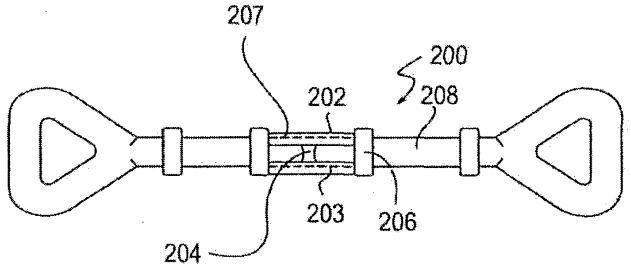


FIG. 23A

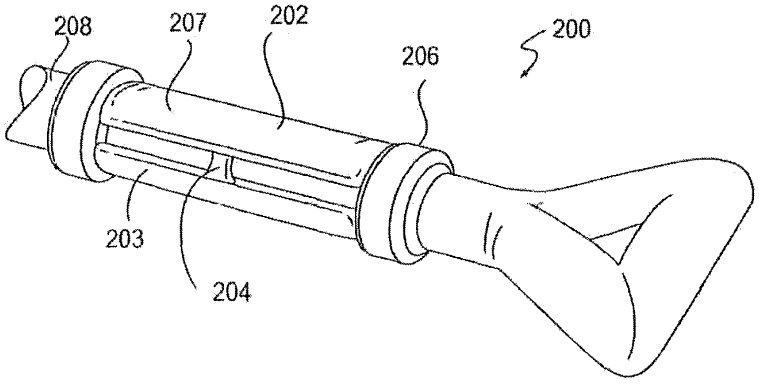


FIG. 23B

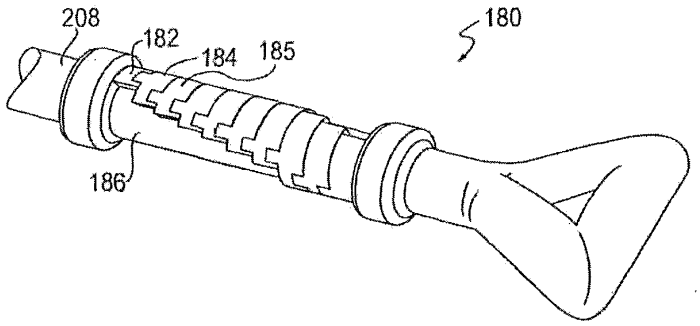


FIG. 24

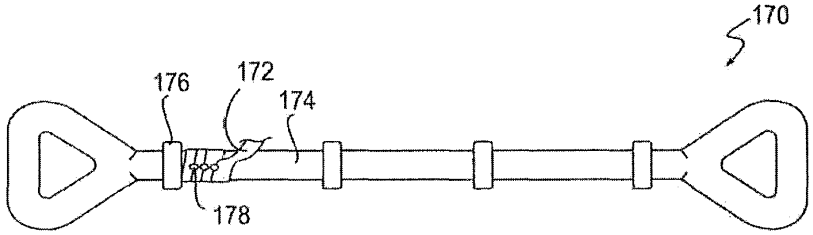


FIG. 25

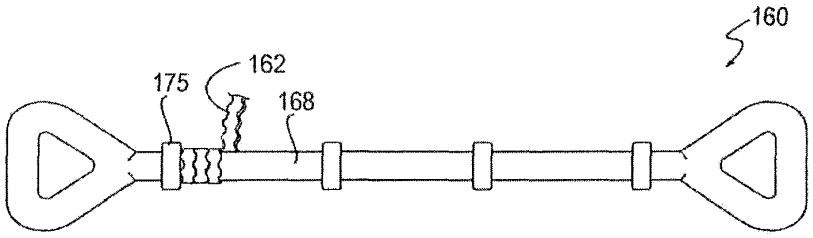


FIG. 26

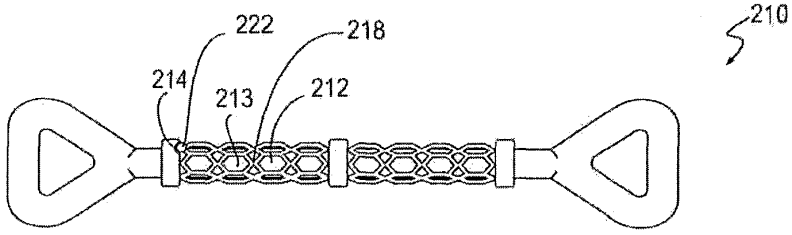


FIG. 27

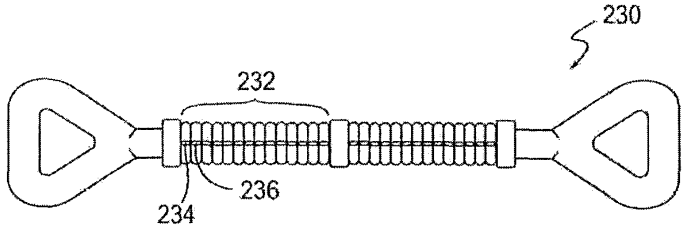


FIG. 28

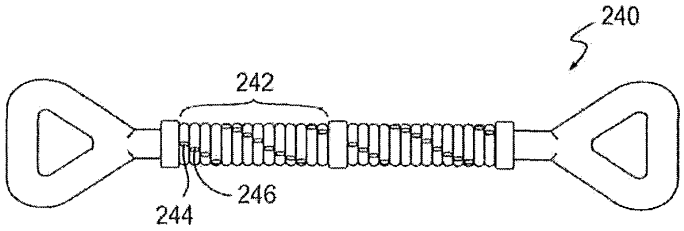


FIG. 29

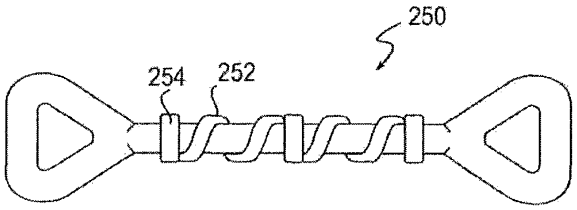


FIG. 30

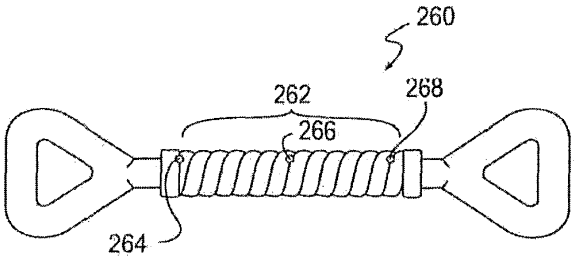


FIG. 31

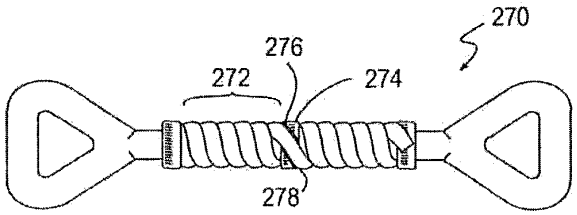


FIG. 32

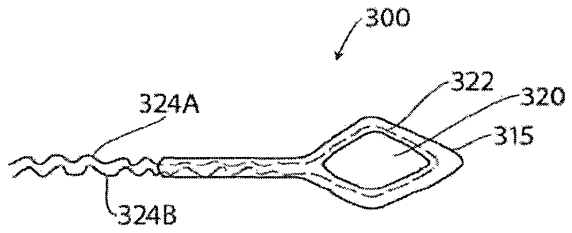


FIG. 33

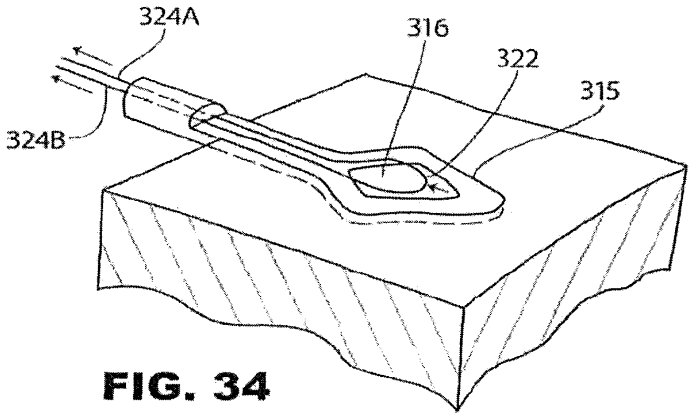


FIG. 34

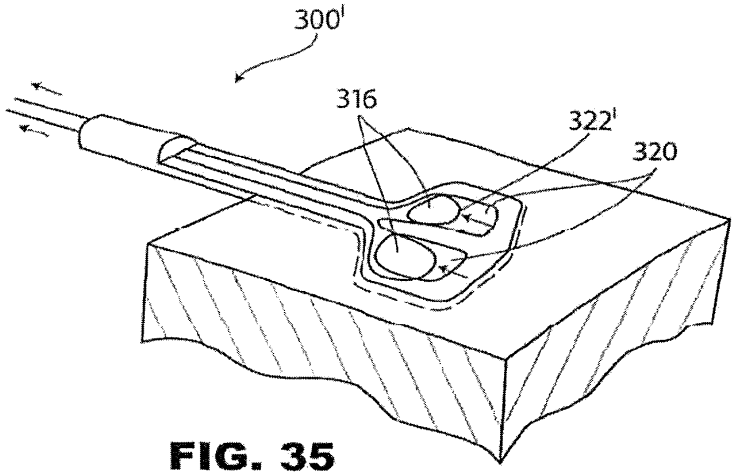


FIG. 35

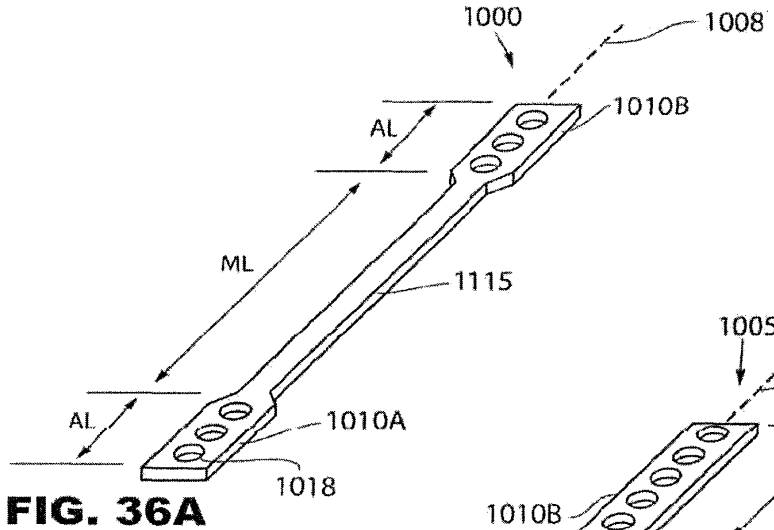


FIG. 36A

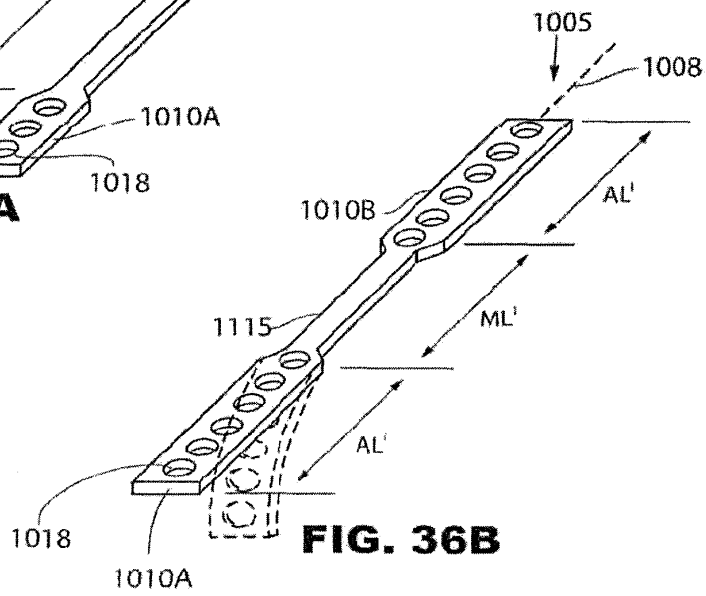


FIG. 36B

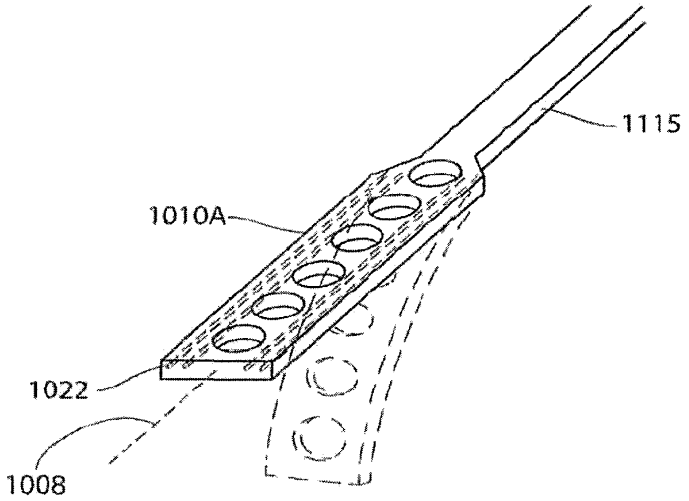


FIG. 37

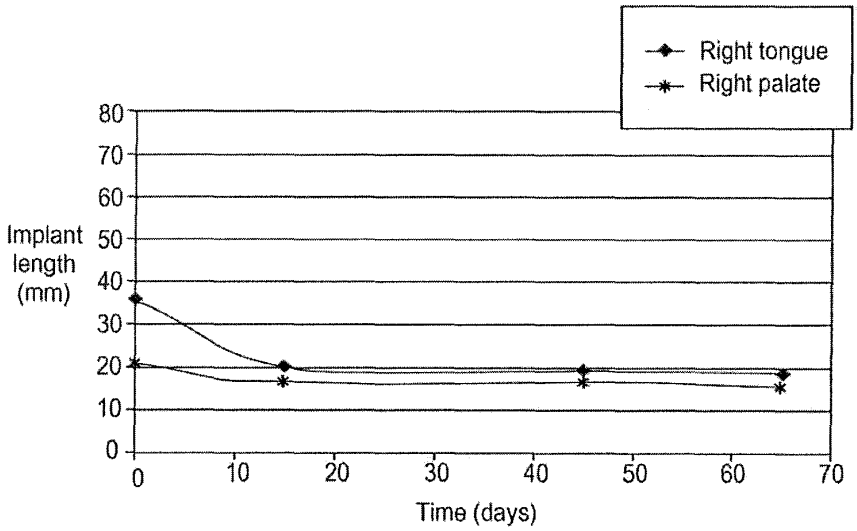


FIG. 38A

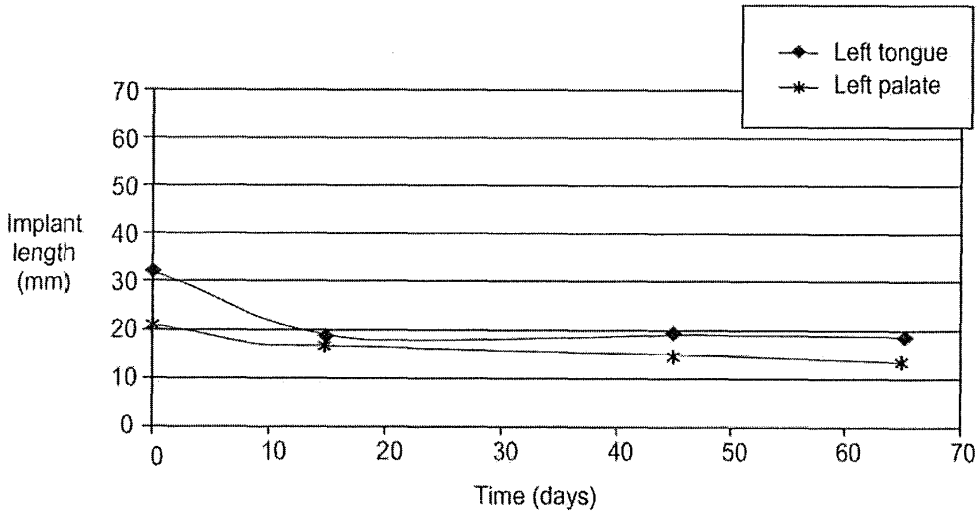


FIG. 38B

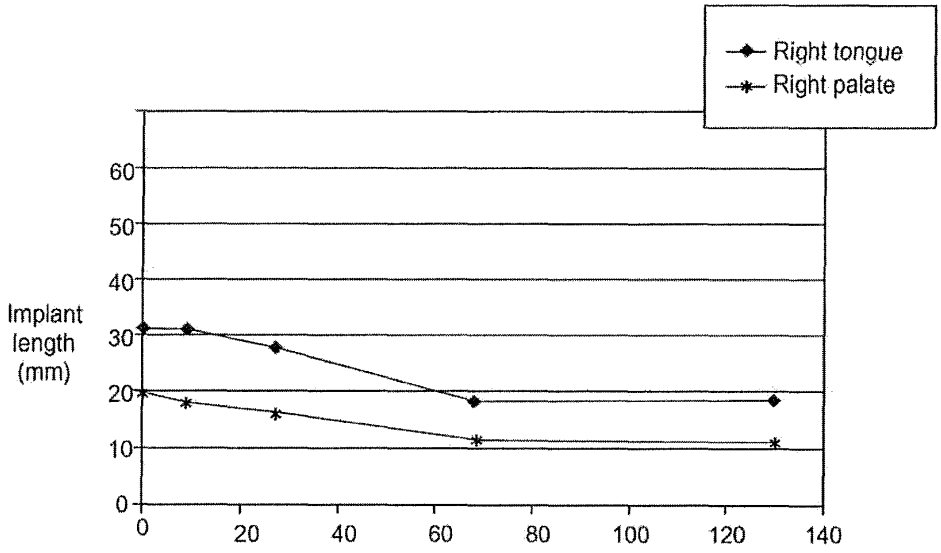


FIG. 38C

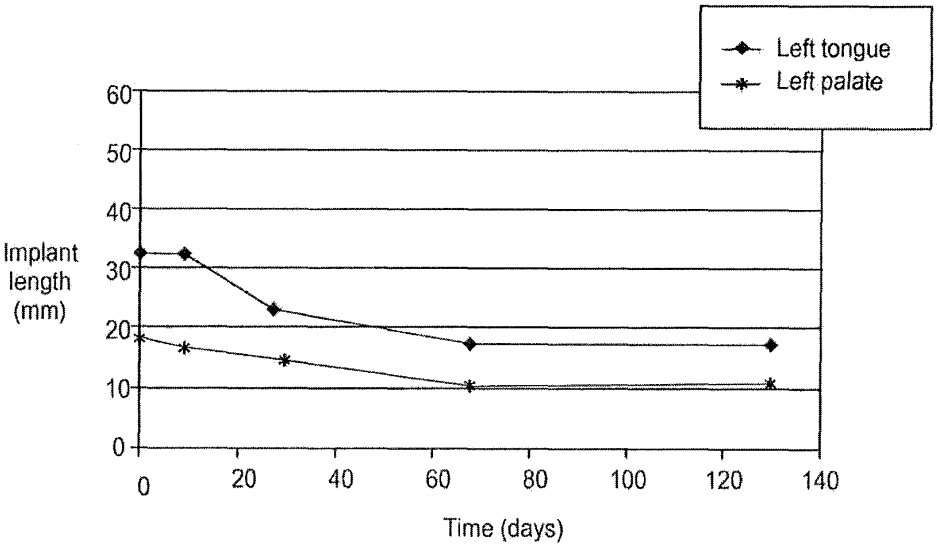


FIG. 38D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/046699

A. CLASSIFICATION OF SUBJECT MATTER

A61F 2/04(2006.01)i, A61F 2/02(2006.01)i, A61F 5/56(2006.01)i, A61B 5/103(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61F 2/04; A61F 5/37; A61F 2/00; A61F 2/06; A61F 5/56; A61F 2/02; A61B 5/103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: sleep apnea, bioerodable, flexibility, coil, spring, wrapping, coupling

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0144421 A1 (GILLIS, E. M. et al.) 16 January 2011 See paragraphs [0043], [0044], [0048], [0059]-[0061] ; claims 2, 3, 23; and figures 5A-C, 6A-B.	21-24
Y		1-20,25-32
Y	US 2011-0308530 A1 (GILLIS, E. M. et al.) 22 December 2011 See paragraphs [0017], [0106]; claim 16.	1-20,25-32
A		21-24
A	US 8096303 B2 (DINEEN, M. et al.) 17 January 2012 See column 13, lines 65-67; column 14, lines 1-20; figure 9A.	1-32
A	US 2010-0163056 A1 (TSCHOPP, K. et al.) 1 July 2010 See paragraphs [0073]-[0075]; figures 1a-b.	1-32
A	US 7793661 B2 (MACKEN, J. A.) 14 September 2010 See abstract; figure 9.	1-32

☐ 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 application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"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
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 October 2013 (07.10.2013)	**07 October 2013 (07.10.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer HAN In Ho Telephone No. +82-42-481-3362

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2013/046699

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 2012-024298 A1	02/02/2012
		US 2013-098374 A1	25/04/2013
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US 2010-0163056 A1	01/07/2010	EP 2204148 A1	07/07/2010
		EP 2204148 B1	28/03/2012
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		JP 2005-349210 A	22/12/2005
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K-FEE SYSTEM GMBH, EX2012, page 2284
NESPRESSO USA, INC. v. K-FEE SYSTEM GMBH
IPR2023-00485, U.S. PATENT 11,230,430

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 January 2014 (03.01.2014)

WIPO | PCT

(10) International Publication Number
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(51) **International Patent Classification**:
H01L 21/66 (2006.01)

(21) **International Application Number**:
PCT/US2013/047691

(22) **International Filing Date**:
25 June 2013 (25.06.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/664,477 26 June 2012 (26.06.2012) US
61/764,435 13 February 2013 (13.02.2013) US

(71) **Applicant**: **KLA-TENCOR CORPORATION** [US/US]; Legal Department, One Technology Drive, Milpitas, California 95035 (US).

(72) **Inventors**: **MANASSEN, Amnon**; Golda Meir 12, 34982 Haifa (IL). **HILL, Andy**; 250 W. El Camino Real #5311, Sunnyvale, California 94087 (US). **KANDEL, Daniel**; 2 Haalon St., 76858 Aseret (IL). **SELA, Ilan**; Taberski Genia 3/13, Ramat Begin, 3475912 Haifa (IL). **BACHAR, Ohad**; 29 He'elah Street, 36576 Timrat (IL). **BRINGOLTZ, Barak**; 13th Hatzanhanim St., Apt. 4, 75712 Rishon Le Tzion (IL).

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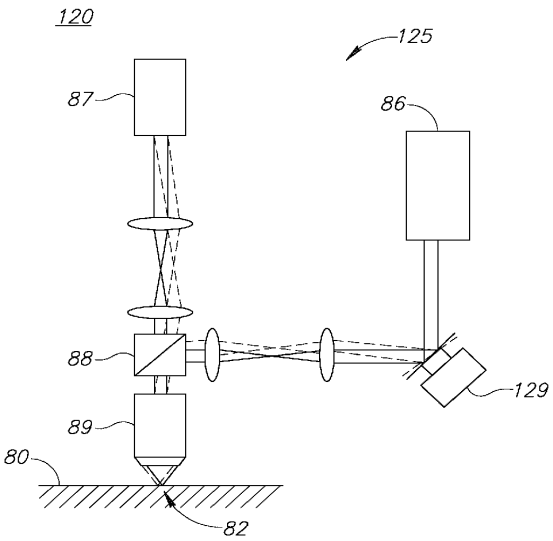
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(54) **Title**: SCANNING IN ANGLE-RESOLVED REFLECTOMETRY AND ALGORITHMICALLY ELIMINATING DIFFRACTION FROM OPTICAL METROLOGY



(57) **Abstract**: Angle-resolved reflectometers and reflectometry methods are provided, which comprise a coherent light source, an optical system arranged to scan a target pattern using a spot of coherent light from the light source to yield realizations of the light distribution in the collected pupil, wherein the spot covers a part of the target pattern and the scanning is carried out optically or mechanically according to a scanning pattern; and a processing unit arranged to generate a composite image of the collected pupil distribution by combining the pupil images. Metrology systems and methods are provided, which reduce diffraction errors by estimating, quantitatively, a functional dependency of measurement parameters on aperture sizes and deriving, from identified diffraction components of the functional dependency which relate to the aperture sizes, correction terms for the measurement parameters with respect to the measurement conditions.

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SCANNING IN ANGLE-RESOLVED REFLECTOMETRY AND ALGORITHMICALLY ELIMINATING DIFFRACTION FROM OPTICAL METROLOGY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application 61/664,477 filed on June 26th 2012 and of U.S. Provisional Patent Application 61/764,435 filed on February 13th 2013, which are incorporated herein by reference in their entirety.

BACKGROUND

1. TECHNICAL FIELD

[0002] The present invention relates to the field of metrology in semiconductor devices and angle-resolved reflectometry, and more particularly, to removal of aperture diffraction effects and to enhancing accuracy and reducing noise in angle-resolved reflectometry.

2. DISCUSSION OF RELATED ART

[0003] Angle-resolved reflectometry is a technique that is used for measuring parameters such as overlay and critical dimension on a test pattern that is printed on a wafer. A cone of light is focused onto the test pattern and the reflectance of the pattern as a function of angle of incidence is collected in a pupil image. The exact intensity distribution of the light in the collected pupil relative to the intensity distribution in the illumination pupil provides the information necessary to extract precise measurements of the test pattern parameters.

[0004] As target sizes become smaller, due to cost and production constraints, applying angle-resolved reflectometry is becoming evermore challenging. The features that make up a test pattern are not uniform throughout the entire test pattern. They invariably

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contain imperfections such as edge roughness, variable line width and side wall slope inconsistencies. These imperfections in the test pattern features scatter or reflect light in a way that modifies the phase and intensity distribution of the light that is collected by the reflectometer.

[0005] Wafer optical metrology tools contain finite size apertures in field planes and in pupil planes. For example, **Figure 6** is a high level schematic illustration of a metrology optical system **90** according the prior art. **Figure 6** illustrates an optical fiber **91** as light source for inspection of a wafer **80** by a pupil image sensor **94**. In this specific schematic example, light travels through an illumination pupil aperture **95A**, an illumination filed aperture **95B**, an objective pupil aperture **95C** and a collection field aperture **95D**.

[0006] These apertures may or may not be apodized and when placed in the plane reciprocal to the plane where the measurement is made, have the following simple purpose. Light arriving into the detector (be it a detector placed in field plane or a detector placed in pupil plane), contains signals from scattering and diffracting elements that are exterior to the metrology target, and that contaminate the sought for ideal signal. One of the aims of such aperture stops is to block this contaminating light. For example, when the signal is collected in pupil plane, a small aperture placed in a field plane on the collection arm, termed a collection field stop, blocks light from the exterior vicinity of the metrology target.

[0007] As the apertures become smaller, the filtering (done in field or in pupil plane) becomes more restrictive and the contaminating light mentioned above is removed in a more efficient way. This, however, comes at the cost of diffractions. Specifically, when the apertures size approaches the spatial coherence length of the radiation, the diffractions off the aperture edges modify the signal in a sizeable amount, and influence the metrology performance. Still, prior art methods suppress diffraction from the field stop by decreasing the spot size (achieved, for example, by means of pupil apodization done in the illumination) and/or choosing the field stop size or shape and a corresponding, judicially chosen region in the collection detector, so that the diffraction effect is small (this may be the case if the larger spot ringing happens on certain areas of the detector).

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BRIEF SUMMARY

[0008] One aspect of the present invention provides an angle-resolved reflectometer comprising: a coherent light source; an optical system arranged to scan a target pattern using a spot of coherent light from the light source to yield a plurality of realizations of a light distribution in a collected pupil, wherein the spot covers a part of the target pattern and the scanning is carried out according to a scanning pattern; and a processing unit arranged to generate a composite image of the collected pupil distribution by combining the plurality of realizations of the light distribution in the collected pupil.

[0009] One aspect of the present invention provides a method comprising estimating, quantitatively, a functional dependency of at least one measurement parameter on a size of at least one aperture in a metrology system; identifying at least one diffraction component of the functional dependency which relates to the size of the at least one aperture; deriving, from the at least one identified diffraction component, a correction term for the at least one measurement parameter with respect to measurement conditions, the measurement conditions comprising specified sizes of the at least one aperture that generate a diffraction error in the at least one measurement parameter; and compensating, computationally, for the diffraction error by applying the derived correction term to the at least one measurement parameter.

[0010] These, additional, and/or other aspects and/or advantages of the present invention are set forth in the detailed description which follows; possibly inferable from the detailed description; and/or learnable by practice of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] For a better understanding of embodiments of the invention and to show how the same may be carried into effect, reference will now be made, purely by way of example, to the accompanying drawings in which like numerals designate corresponding elements or sections throughout.

[0012] In the accompanying drawings:

Figure 1 is a high level schematic diagram illustrating an angle-resolved reflectometer with optical scanning, according to some embodiments of the invention;

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Figure 2 is a high level schematic diagram illustrating an angle-resolved reflectometer implementing a scanning pattern, according to some embodiments of the invention;

Figure 3 is a high level schematic diagram illustrating scanning patterns having difference sizes and densities, according to some embodiments of the invention;

Figure 4 is a high level schematic block diagram illustrating various parameters and controlled variables of a scanning angle-resolved reflectometer, according to some embodiments of the invention;

Figure 5 is a high level schematic flowchart illustrating an angle-resolved reflectometry method, according to some embodiments of the invention;

Figure 7 is a high level schematic illustration of a generic dependency of some measurable variable termed "Quantity^{raw}" on an aperture size in the system, according to some embodiments of the invention;

Figure 8 is a high level schematic flowchart illustrating a method of algorithmically eliminating diffraction from optical metrology, according to some embodiments of the invention;

Figure 9 is a high level schematic block diagram illustrating a metrology system, according to some embodiments of the invention;

Figure 10A is a schematic diagram illustrating an example for the way the inaccuracy in a scatterometry overlay measurement may depend on the size of the collection field stop, according to some embodiments of the invention;

Figure 10B is a schematic diagram illustrating an example for the way the inaccuracy in a scatterometry overlay measurement depends on the size of the collection field stop for two different values of the true overlay, according to some embodiments of the invention;

Figure 11A is a schematic diagram illustrating an example for the way the correction method using a first type of calibration reduces the overlay measurement error, according to some embodiments of the invention; and

Figure 11B is a schematic diagram illustrating an example for the way the correction method using a second type of calibration reduces the overlay measurement error, according to some embodiments of the invention.

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DETAILED DESCRIPTION

[0013] Prior to setting forth the detailed description, it may be helpful to set forth definitions of certain terms that will be used hereinafter.

[0014] The terms "target" or "metrology target" as used herein in this application refer to any structure that is used for metrology needs. Targets may be part of any layer in the lithographic process, and targets may include different structures on the same layer or on different layers.

[0015] The terms "speckle pattern" or "speckle"as used herein in this application refer to an intensity pattern of an optical signal that is produced by interference of at least two wavefronts, and generally to a source of measurement error resulting from interfering wavefronts at the sensor plane.

[0016] With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

[0017] Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is applicable to other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0018] **Figure 1** is a high level schematic diagram illustrating an angle-resolved reflectometer **120** with optical scanning, according to some embodiments of the invention. **Figure 2** is a high level schematic diagram illustrating angle-resolved

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