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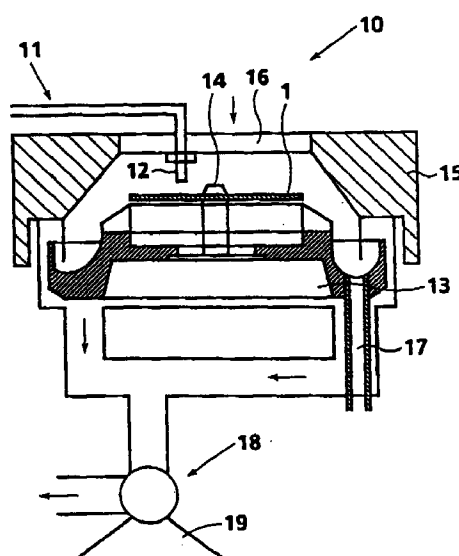
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(54) **Spin-coating apparatus for preparing optical discs**

(57) A spin-coating apparatus (10) for preparing optical discs (1) is composed of an applying device equipped with a nozzle (12) having a pointed end for giving a coating liquid onto a disc substrate (1), a rotatable spinner head (13) for keeping the substrate (1) horizontally, a round guard wall (15) provided around the spinner head (13) which has an opening (16) on its top and keeps the applied coating liquid within the guard wall (15), and an air exhaust system (18), wherein the nozzle (12) has a surface of polytetrafluoroethylene at least at the pointed end and on an inside and outside walls following the pointed end at a length of 1 mm or more.

**FIG. 1**



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**Description**FIELD OF THE INVENTION

5 **[0001]** This invention relates to a spin-coating apparatus for preparing optical discs.

BACKGROUND OF THE INVENTION

10 **[0002]** Hitherto, a spin-coating method has been widely used for preparing optical discs. The spin-coating method comprises the steps of dropping a coating liquid onto a central part of a rotating substrate, spreading the liquid outward by centrifugal force to form a coating film on the substrate, splashing off excess of the liquid from the edge of the substrate, and then drying the coating film by evaporating the solvent. Examples of optical discs prepared by the spin-coating method are: an optical disc of CD-R type comprising a disc-shaped transparent substrate (hereinafter referred to as "disc substrate" or simply "substrate"), a recording dye layer, a light-reflecting layer, and a protective layer overlaid in order; an optical disc of DVD-R type formed by combining a multi-layered composite (comprising a disc substrate, a recording dye layer, a light-reflecting layer, and if desired, a protective layer overlaid in order) and another disc substrate (protective substrate) with an adhesive so that the recording layer may be placed inside; and an optical disc of DVD-R type formed by combining a pair of the multi-layered composites with an adhesive so that each recording layer may be placed inside. In preparing these optical discs, the recording dye layer and the protective layer are often formed by the spin-coating method. In Japanese Patent Publication No. 7 (1995)-118094, the preparation process of CD-R type optical discs is described in detail.

**[0003]** The spin-coating method is generally performed by means of an apparatus described below.

25 **[0004]** A spin-coating apparatus generally comprises an applying device, a spinner head, a round guard wall and an exhaust system. The applying device comprises a nozzle equipped with a pressure tank and a regulating valve for adjusting the amount of a drop of the coating liquid which is given through the nozzle onto the surface of a disc substrate. The spinner head is placed below the applying device to hold the substrate horizontally with a detachable mount, and is rotatable around its axis by means of a driving motor. In the apparatus, the coating liquid is dropped from the nozzle onto the rotating substrate horizontally held on the spinner head, and then spread outward to form a coating film on the substrate. The excess of the liquid is splashed off from the edge of the substrate by centrifugal force, and then the coating film is dried by evaporating the solvent. In order to shield the surroundings from the thus splashed excess liquid, the guard wall is provided around the spinner head and the wall has an opening on its top. In the exhaust system, air is introduced from the opening on the top, made to flow over the surface of the substrate, and then exhausted from a space below the spinner head. Since the exhaust system has an exhaust fan and a regulating valve for adjusting the amount of the exhausted air, the conditions for drying the coating film can be easily varied by adjusting the amount of the exhausted air (i.e., by adjusting the flow rate of the air).

35 **[0005]** The nozzle of the applying device is generally made of stainless steel. However, if the coating liquid is a dye solution for preparing a recording dye layer, the nozzle of stainless steel exhibits a small contact angle to the solution. This means that the surface of the nozzle is well wetted with the solution and therefore that the solution well attaches onto the pointed end (leading end) of the nozzle. As shown in Figure 5, the solution thus attaching onto the pointed end is liable to easily dry to deposit a solid dye (sediment 53) while the apparatus is continuously used for a long time. The sediment formed at the pointed end often causes troubles. For example, the sediment may fall onto the substrate to damage a formed film, and further it may choke the nozzle to prevent the coating liquid from dropping smoothly. In order to avoid these troubles, some known apparatuses are equipped with cleaning means by which the pointed end of the nozzle is washed and dried. However, the apparatus having the cleaning means requires a complicated system. In practice, the pointed end of the nozzle is regularly cleaned while the production line is stopped at regular intervals. However, the regular stoppage of the production line lowers the production efficiency, and further film-forming errors are liable to occur while the line is repeatedly stopped and resumed.

SUMMARY OF THE INVENTION

50 **[0006]** Accordingly, it is an object of the present invention to provide a spin-coating apparatus in which the coating liquid hardly attaches onto the pointed end of the nozzle and hence which can be continuously used for forming a coating film for a long time. In the spin-coating apparatus of the invention, the coating liquid is prevented from attaching onto the pointed end of the nozzle without either providing the cleaning means or stopping the production line at regular intervals.

55 **[0007]** The inventors had studied about the nozzle of the applying device, and found the following fact. If the pointed end of the nozzle has a surface made of polytetrafluoroethylene (Teflon), the coating liquid hardly attaches onto the end. Consequently, the apparatus having such nozzle can keep producing optical discs efficiently for a long time without the

troubles.

[0008] The present invention resides in a spin-coating apparatus for preparing optical discs, comprising

an applying device equipped with a nozzle having a pointed end for giving a coating liquid onto a disc-shaped transparent substrate,  
 a spinner head which is placed below the applying device to keep the substrate horizontally and which is rotatable around its axis,  
 a guard wall provided around the spinner head which has an opening on its top and keeps therewithin the coating liquid which is given onto the rotating substrate on the spinner head, spreads outward, and then splashes around the substrate, and  
 an exhaust system in which air is introduced from the opening, made to flow over the substrate, and then exhausted from a space below the spinner head;  
 wherein the nozzle has a surface made of polytetrafluoroethylene at least at the pointed end and on an inside and outside walls following the pointed end at a length of longer than 1 mm.

[0009] Preferred embodiments of the invention are as follows.

(1) The nozzle is made of stainless steel, and its surface of the wall is covered with polytetrafluoroethylene at least at the pointed end and on the inside and outside walls following the pointed end at a length of longer than 1 mm (preferably longer than 5 mm, more preferably longer than 10 mm).

(2) The nozzle is made of stainless steel, and the whole surface of the nozzle is completely covered with polytetrafluoroethylene.

(3) The coating liquid is a dye solution.

## BRIEF DESCRIPTION OF DRAWINGS

[0010]

Figure 1 shows a schematic sectional view of a spin-coating apparatus of the invention.

Figure 2 shows schematic views of an applying device of the invention. In Figure 2, (a) is a plan view and (b) is a front elevation.

Figure 3 shows a schematic sectional view of an example of the nozzle having the pointed end which is covered with polytetrafluoroethylene

Figure 4 shows a partial schematic sectional view of an optical disc comprising a disc-shaped transparent substrate, a recording dye layer, a light-reflecting layer, and a protective layer overlaid in order.

Figure 5 is a schematic view showing a solid dye (sediment) deposited at the pointed end of a known nozzle.

## DETAILED DESCRIPTION OF THE INVENTION

[0011] The spin-coating apparatus of the invention comprises an applying device, a spinner head, a guard wall and an exhaust system. The applying device has a specific nozzle. Referring to the attached drawings, the spin-coating apparatus of the invention is described below in detail.

[0012] Figure 1 shows a schematic sectional view of a spin-coating apparatus of the invention. As shown in Figure 1, the spin-coating apparatus 10 comprises applying device 11, spinner head 13, guard wall 15 and exhaust system 18.

The applying device 11 comprises nozzle 12 equipped with a pressure tank (not shown in the figure) and a regulating valve (not shown in the figure) for adjusting the amount of a drop of coating liquid which is given through the nozzle 12 onto the surface of the disc substrate 1. In the apparatus 10, the applying device 11 can be moved from a waiting position to the predetermined position over the substrate 1 by means of a handling mechanism (not shown in the figure). The spinner head 13 is placed below the applying device 11 to hold the substrate 1 horizontally with detachable mount 14, and is rotatable around the axis with a driving motor (not shown in the figure). In the process for forming a coating film, the coating liquid is dropped from the nozzle 12 of the applying device 11 onto the rotating substrate 1 horizontally supported by the spinner head 13, and then spread outward by centrifugal force to form a coating film on the substrate 1. The excess of the liquid is splashed off from the edge of the substrate 1, and the coating film is dried by removing the solvent. In order to keep the surroundings from the thus splashed liquid, the guard wall 15 is provided around the spinner head 13 and the wall has an opening 16 on its top position. The excess liquid collected on the guard wall 15 is introduced into the drain 17. In the exhaust system 18, air is aspirated from the opening 16, made to flow over the surface of the substrate 1, and then exhausted from a space below the spinner head 13. Since the exhaust system 18 has an exhaust fan 19 and a regulating valve (not shown in the figure) for adjusting the amount of the exhausted air, the con-

ditions for drying the coating film can be easily varied by adjusting the amount of the exhausted air (i.e., by adjusting the flow rate of the air).

[0013] The applying device having the specific nozzle is described below in detail.

[0014] Figure 2 shows schematic views of an applying device of the invention. In Figure 2, (a) is a plan view and (b) is a front elevation. Figure 3 also shows a schematic sectional view of a preferred example of the nozzle. In the nozzle 22 of the applying device 21 according to the invention, the pointed end and both the inside and the outside within not less than 1 mm of the pointed end have surfaces made of polytetrafluoroethylene. Typical examples of the nozzle preferably used for the invention are: a nozzle in which the pointed end and the body within not less than 1 mm of the pointed end are made of polytetrafluoroethylene; and a nozzle (shown in Figure 3) in which the pointed end 23 and both of the inner wall surface 24 and the outer wall surface 25 within not less than 1 mm of the pointed end are covered with polytetrafluoroethylene. The former nozzle is, for example, prepared in the following manner. First, the nozzle body except for the end part is beforehand made of stainless steel. After that, the end part (the pointed end and the body within not more than 5 mm of the pointed end) is made of polytetrafluoroethylene. This structure is practically preferred in consideration of strength of the nozzle. In the nozzle shown Figure 3, the pointed end and the nozzle body within not less than 10 mm of the pointed end are preferably covered with polytetrafluoroethylene. More preferably, the whole surface of the nozzle is completely covered with polytetrafluoroethylene. The thickness of the coating polytetrafluoroethylene covering layer is not particularly restricted, but usually in the range of 5 to 500  $\mu\text{m}$ . As described above, the body of the nozzle is preferably made of stainless steel. The inner diameter of the nozzle generally is in the range of 0.5 to 1.0 mm.

[0015] The following is a detailed description of the process for preparing optical discs employing the spin-coating apparatus having the applying device equipped with the nozzle of the invention.

[0016] A typical optical disc prepared in the process is shown in Figure 4. The disc 40 in Figure 4 comprises a disc-shaped transparent substrate 1, a recording dye layer 2, a light-reflecting layer 3, and a protective layer 4 overlaid in this order.

[0017] Examples of materials for the substrate include polycarbonate, acrylic resins such as polymethyl methacrylate, vinyl chloride resins such as polyvinyl chloride and vinyl chloride copolymer, epoxy resins, amorphous polyolefins, and polyesters. These materials can be employed in combination, if desired. Polycarbonate is most preferred from the viewpoints of humidity resistance, dimensional stability and economical cost.

[0018] On the surface of the substrate, a pregroove for tracking or giving address signals is preferably formed. The pregroove is preferably formed directly on the surface of the substrate when the substrate is molded from polymer material (such as polycarbonate) by injection or extrusion. The pregroove preferably has a depth in the range of 0.01 to 0.3  $\mu\text{m}$  and a half-width of 0.2 to 0.9  $\mu\text{m}$ .

[0019] The recording dye layer is formed on the disc substrate in the following manner by means of the spin-coating apparatus of the invention.

[0020] First, the disc substrate 1 is installed on the mount 14 of the spinner head 13 shown in Figure 1. The substrate 1 is horizontally kept on the spinner head 13. The coating liquid supplied from the pressure tank (not shown in the figure) is introduced to the regulating valve (not shown in the figure) so that the amount may be adjusted to the predetermined volume, and then dropped through the nozzle 12 onto the central part of the substrate 1. As described above, since the nozzle 12 of the invention has the surface of polytetrafluoroethylene at the pointed end and on the inside and the outside walls within not less than 1 mm from the pointed end, the coating liquid hardly adheres to the end. Therefore, the coating film can be smoothly formed without troubles caused by the deposited dye. The coating liquid is generally prepared by dissolving a dye in a proper solvent in an amount of 0.01 to 15 wt.%, preferably 0.1 to 10 wt.%, more preferably 0.5 to 5 wt.%, further preferably 0.5 to 3 wt.%.

[0021] In the apparatus, the spinner head 13 is made to rotate at a high speed by a driving motor. The coating liquid is dropped onto the central part of the rotating substrate 1, spread outward to the edge of the substrate 1, and then splashed off from the edge by centrifugal force. The splashed liquid bumps on the guard wall 15 to gather in a gutter provided at the foot of the wall, and the gathered liquid is removed through the drain 17. During or after the procedure for forming the coating film, the film is dried. The coating film (dye recording layer) generally has a thickness of 20 to 500 nm, preferably 50 to 300 nm.

[0022] The dyes used for the recording dye layer are not particularly restricted. Examples of the dyes include cyanine dye, phthalocyanine dye, imidazoquinoline dyes, pyrylium/thiopyrylium dyes, azulenium dyes, squalilium dyes, metal complex dyes such as Ni complex and Cr complex, naphthoquinone dyes, anthraquinone dyes, indophenol dyes, indoaniline dyes, triphenylmethane dyes, merocyanine dyes, oxonol dyes, aminium/diiminium dyes, and nitroso compounds. Preferred are cyanine dye, phthalocyanine dye, azulenium dyes, squalilium dyes, oxonol dyes, and imidazoquinoline dyes.

[0023] Examples of the solvent used for the coating liquid for the dye recording layer include esters such as butyl acetate and cellosolve acetate; ketones such as methyl ethyl ketone, cyclohexanone and methyl isobutyl ketone; chlorinated hydrocarbons such as dichloromethane, 1,2-dichloroethane and chloroform; amides such as dimethylformamide;

hydrocarbons such as cyclohexane; ethers such as tetrahydrofuran, diethyl ether and dioxane; alcohols such as ethanol, n-propanol, isopropanol, n-butanol, and diacetone alcohol; fluorine atom-containing solvents such as 2,2,3,3-tetrafluoropropanol; and glycol ethers such as ethyleneglycol monomethyl ether, ethyleneglycol monoethyl ether and propyleneglycol monomethyl ether. These solvents can be employed in combination in consideration of the solubility of the used dye. Preferred are fluorine atom-containing solvents such as 2,2,3,3-tetrafluoropropanol.

**[0024]** The coating liquid may contain, if desired, not only an anti-fading agent and a binder but also auxiliary additives such as an oxidation inhibitor, a UV absorber, a plasticizer and a lubricant.

**[0025]** Examples of the anti-fading agents include nitroso compounds, metal complex compounds, diimmonium salts and aminium salts. Those examples are described in Japanese Patent Provisional Publications No. H2(1990)-300288, No. H3(1991)-224793 and No. H4(1992)-146189.

**[0026]** Examples of the binders include natural-origin polymers such as gelatin, cellulose derivatives, dextran, rosin and rubber; hydrocarbon polymer resins such as polyethylene, polypropylene, polystyrene and polyisobutylene; vinyl polymers such as polyvinyl chloride, polyvinylidene chloride, and vinyl chloride-vinyl acetate copolymer; acrylate polymers such as polymethyl acrylate and polymethyl methacrylate; polyvinyl alcohol, chlorinated polyethylene; epoxy resins; butyral resins, rubber derivatives, and thermosetting resins such as prepolymers of phenol-formaldehyde. The binder is generally used in an amount of not more than 20 weight parts, preferably not more than 10 weight parts, more preferably not more than 5 weight parts based on 100 parts of the dye.

**[0027]** The substrate may have an undercoating layer on its surface on the recording layer side, so as to enhance surface smoothness and adhesion and to keep the dye recording layer from deterioration.

**[0028]** Examples of the material for the undercoating layer include polymers such as polymethyl methacrylate, acrylate-methacrylate copolymer, styrene-maleic anhydride copolymer, polyvinyl alcohol, N-methylolacrylamide, styrene-vinyltoluene copolymer, chloro-sulfonated polyethylene, nitrocellulose, polyvinyl chloride, chlorinated polyolefin, polyester, polyimide, vinyl acetate-vinyl chloride copolymer, ethylene vinyl acetate copolymer, polyethylene, polypropylene and polycarbonate; and surface treating agents such as a silane-coupling agent. The undercoating layer can be formed by applying a coating solution (in which one or more of the above-mentioned materials are dissolved or dispersed) onto the surface of the substrate by the known coating methods such as spin-coat, dip-coat, and extrusion-coat. The undercoating layer generally has a thickness of 0.005 to 20  $\mu\text{m}$ , preferably 0.01 to 10  $\mu\text{m}$ .

**[0029]** On the dye recording layer, the light-reflecting layer is placed so as to enhance the light-reflection in the course of reproduction of information. The light-reflecting material to be used for the formation of the light-reflecting layer should show a high reflection to the laser light. Examples of the light-reflecting materials include metals and sub-metals such as Mg, Se, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Si, Ge, Te, Pb, Po, Sn, and Bi. Stainless steel film is also employable. Preferred light-reflecting materials are Cr, Ni, Pt, Cu, Ag, Au, Al and stainless steel film. These materials can be employed singly, in combination, or in the form of alloy. Au, Ag and their alloys are particularly preferred. The light-reflecting layer can be formed on the recording layer by vacuum deposition, sputtering, or ion-plating. The thickness of the light-reflecting layer generally is 10 to 800 nm, preferably 20 to 500 nm, more preferably 50 to 300 nm.

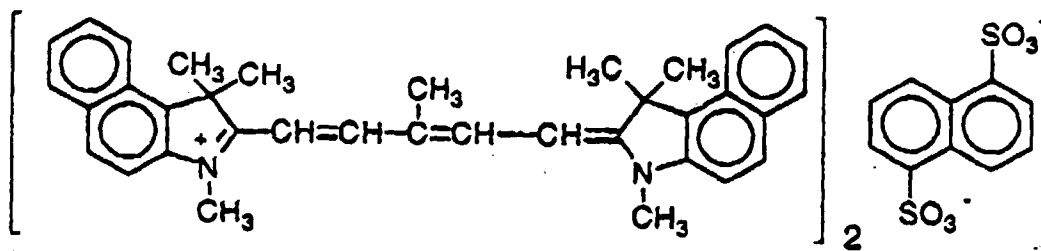
**[0030]** On the light-reflecting layer, a protective layer can be placed so as to protect the recording layer from chemical deterioration or physical damage. The protective layer can be also placed on the substrate on the face not having the recording layer so as to enhance the scratch resistance and the moisture resistance of the disc. The protective layer can be formed of inorganic materials such as  $\text{SiO}$ ,  $\text{SiO}_2$ ,  $\text{MgF}_2$ ,  $\text{SnO}_2$ , and  $\text{Si}_3\text{N}_4$ ; or organic materials such as thermoplastic resins, thermosetting resins, and UV curable resins.

**[0031]** The protective layer can be formed on the light-reflecting layer and/or the substrate by laminating a film of plastic material with an adhesive. The inorganic material can be also placed on the light-reflecting layer and/or the substrate by vacuum deposition or sputtering. Otherwise, the organic polymer material can be coated in the form of a solution containing the polymer material and dried to give the protective layer. For example, the UV curable resin is dissolved in a solvent and coated on the light-reflecting layer and/or the substrate, and cured by applying ultra-violet rays to the coated solution. The coating solution may include various additives such as an anti-static agent, an oxidation inhibitor, and a ultra-violet absorber. The protective layer generally has a thickness of 0.1 to 100  $\mu\text{m}$ .

**[0032]** In the process for producing an optical disc, the undercoating layer and/or the protective layer may be formed by means of the spin-coating apparatus of the invention in the manner described above for forming the recording dye layer.

## Example and Comparison Example

## [Comparison Example 1]



[0034] The cyanine dye having the above formula was dissolved in 2,2,3,3-tetrafluoropropanol to give a coating solution for preparing a recording dye layer (dye content: 2.65 % wt./vol.).

[0035] Independently, a polycarbonate transparent substrate (diameter: 120 mm, thickness: 1.2 mm, Panlight AD5503 (trade name), available from Teijin Limited) was prepared. The substrate had a spirally formed pregroove (track pitch: 1.6  $\mu\text{m}$ , width: 0.5  $\mu\text{m}$ , depth: 0.17  $\mu\text{m}$ ) which was produced by the injection molding.

[0036] The coating solution was then applied onto the substrate surface having the pregroove thereon by means of a conventional spin-coating apparatus comprising an applying device equipped with a stainless steel nozzle (inner diameter: 0.8  $\mu\text{m}$ ). The rotation of the spinner head was varied from 300 r.p.m. to 2000 r.p.m., to form a recording dye layer (thickness at the groove: approx. 200 nm). The conditions for forming the layer were as follows:

room temperature and humidity: 23°C and 50%RH,  
 temperature of the solution: 23°C,  
 temperature of the substrate: 23°C, and  
 flow rate of the air: 0.8 m/second.

[0037] On the coated dye layer, a light-reflecting layer (thickness: 100 nm) of gold was provided by sputtering. Subsequently, a UV curable photopolymer (UV curable agent: SD-220, available from Dainippon Ink & Chemicals, Inc.) was coated on the light-reflecting layer by means of the conventional spin-coating apparatus. The rotation of the spinner head was varied from 300 r.p.m. to 2,000 r.p.m. to give a coated layer. The coated layer was irradiated with ultra-violet rays for curing to form a protective layer (thickness: 8  $\mu\text{m}$ ).

[0038] Thus, an optical disc of CD-R type comprising the substrate, the dye recording layer, the light-reflecting layer and the protective layer overlaid in order was produced.

## [Example 1]

[0039] The procedure of Comparison Example 1 was repeated except for using the spin-coating apparatus of the invention (shown in Figure 1) comprising an applying device equipped with a nozzle (material of the body: stainless steel, inner diameter: 0.8  $\mu\text{m}$ ) having the whole wall surface completely covered with polytetrafluoroethylene, in place of the above conventional apparatus. Thus, an optical disc of CD-R type was produced.

## [Evaluation of Spin-Coating Apparatuses]

[0040] After 300 discs were continuously produced in accordance with Comparison Example 1, a deposited solid dye (sediment 53) was observed at the pointed end of the nozzle as shown in Figure 5. In contrast, the nozzle employed in Example 1, no sediment was observed even after 300 discs were continuously produced. Consequently, it was confirmed that 300 discs of high quality were continuously produced without any trouble by means of the apparatus of the invention.

## Claims

## 1. A spin-coating apparatus for preparing optical discs, comprising

5 an applying device equipped with a nozzle having a pointed end for giving a coating liquid onto a disc-shaped transparent substrate,  
 a spinner head which is placed below the applying device to keep the substrate horizontally and which is rotatable around its axis,  
 10 a guard wall provided around the spinner head which has an opening on its top and keeps therewithin the coating liquid which is given onto the rotating substrate on the spinner head, spreads outward, and then splashes around the substrate, and  
 an exhaust system in which air is introduced from the opening, made to flow over the substrate, and then exhausted from a space below the spinner head;  
 15 wherein the nozzle has a surface made of polytetrafluoroethylene at least at the pointed end and on an inside and outside walls following the pointed end at a length of longer than 1 mm.

2. The spin-coating apparatus of claim 1, wherein the nozzle is made of stainless steel, and its surface of the wall is covered with polytetrafluoroethylene at least at the pointed end and on the inside and outside walls following the pointed end at a length of longer than 1 mm.

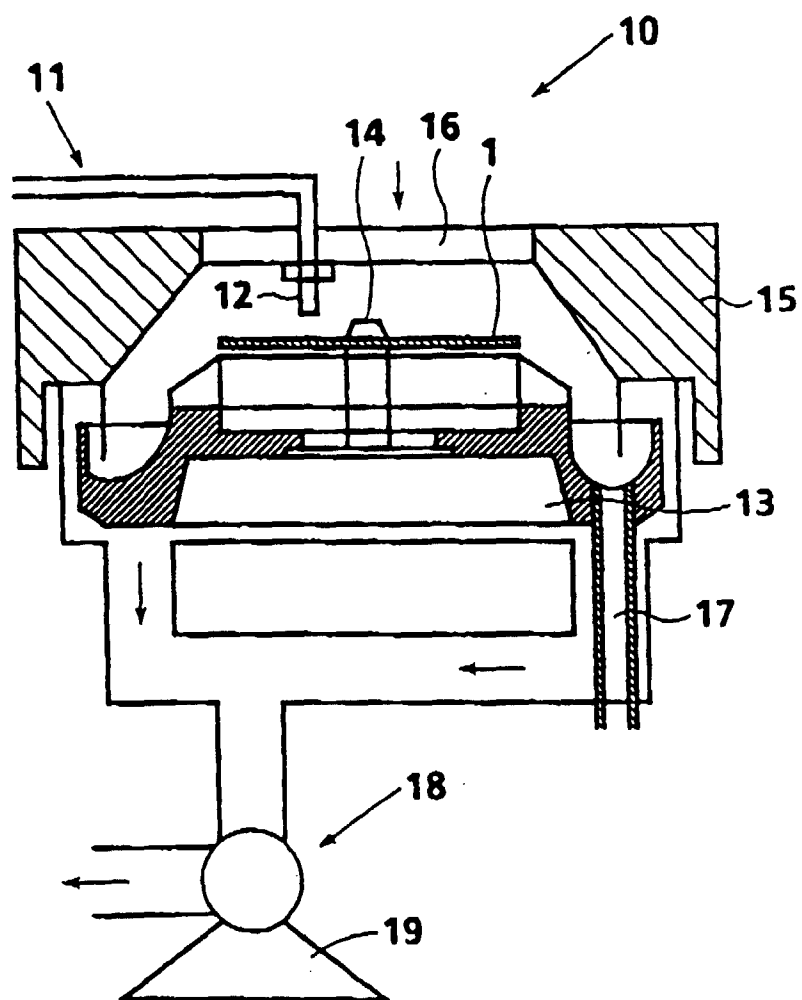
3. The spin-coating apparatus of claim 2, wherein the nozzle of stainless steel is covered on its surfaces of the walls with polytetrafluoroethylene at least at the pointed end and on the inside and outside walls following the pointed end at a length of longer than 5 mm.

4. The spin-coating apparatus of claim 2, wherein the nozzle of stainless steel is covered at the pointed end and on its whole surfaces of the walls with polytetrafluoroethylene.

5. The spin-coating apparatus of claim 1, wherein the nozzle is made of stainless steel, and its surface of the wall is covered with a polytetrafluoroethylene layer having a thickness of 5 to 500  $\mu\text{m}$ .

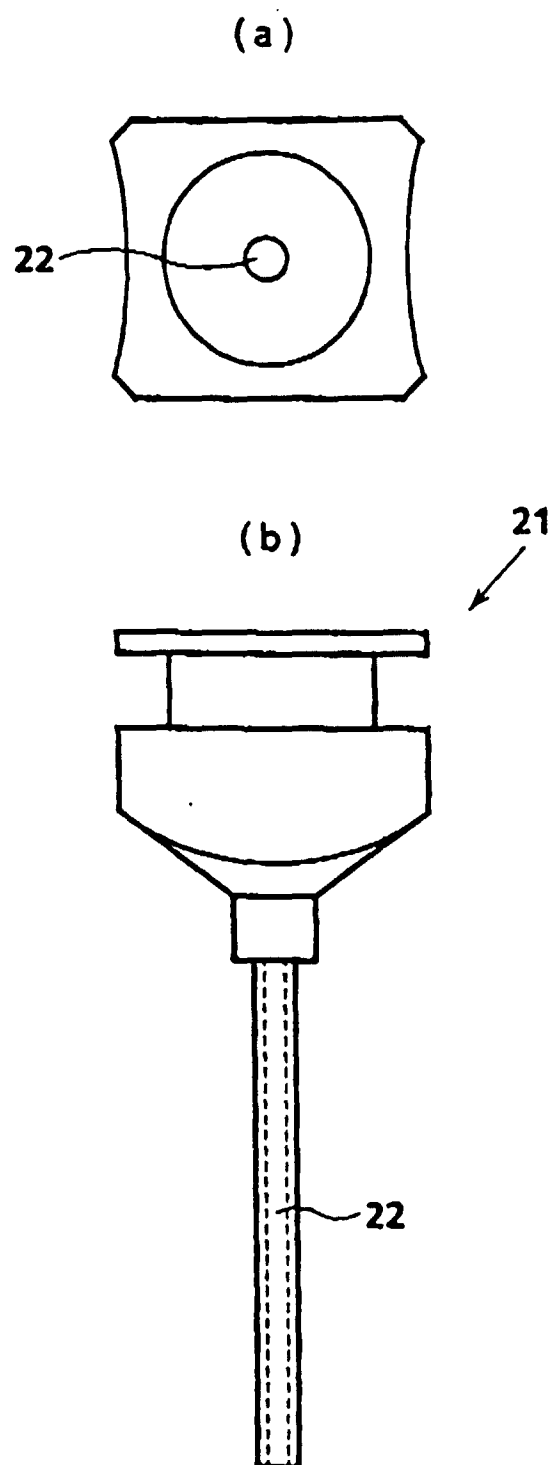
6. The spin-coating apparatus of claim 1, wherein the nozzle has an inner diameter of 0.5 to 1.0 mm.

FIG. 1

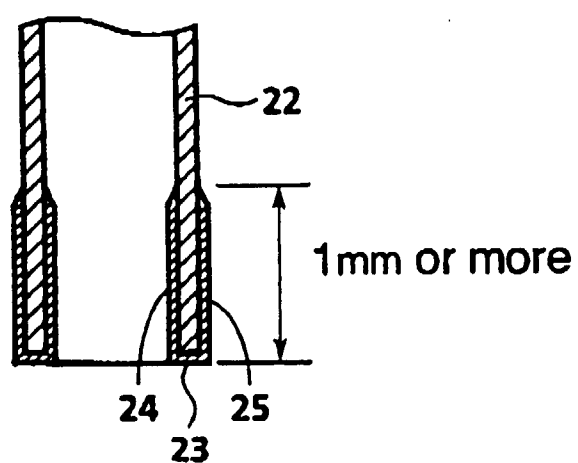




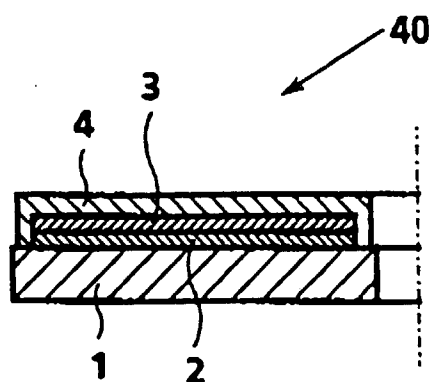
**FIG. 2**



**FIG. 3**



**FIG. 4**



**FIG. 5**

