(11) **EP 2 564 939 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

06.03.2013 Bulletin 2013/10

(51) Int Cl.: **B05C** 3/18 (2006.01) **B05C** 11/02 (2006.01)

B05C 5/02 (2006.01)

(21) Application number: 12181701.9

(22) Date of filing: 24.08.2012

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

(30) Priority: 26.08.2011 JP 2011185119

(71) Applicant: Fujifilm Corporation

Minato-ku

Tokyo 106-8620 (JP)

(72) Inventors:

 Oshima, Atsushi Shizuoka, 421-0396 (JP)

Sone, Nobuyuki
 Shizuoka, 421-0396 (JP)

 Koseki, Rie Shizuoka, 421-0396 (JP)

(74) Representative: HOFFMANN EITLE

Patent- und Rechtsanwälte

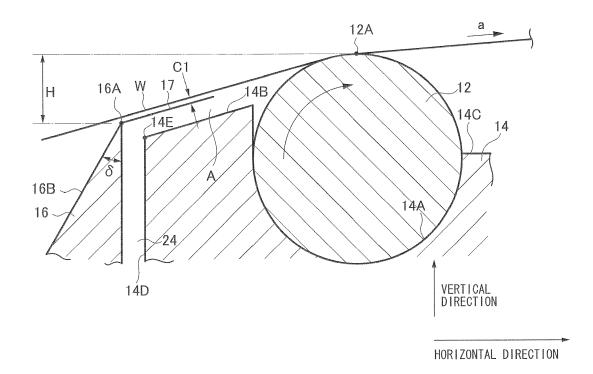
Arabellastrasse 4 81925 München (DE)

(54) Coating apparatus and coating method

(57) When coating liquid is applied to a web (W) in a bar coater while the web (W) is being run, the coating liquid is prevented from becoming solidified to cause a streak failure or result in occurrence of a foreign material adhesion where a solidified material adheres to a coated

surface in a gas-liquid-solid interface on an upstream side of a bar (12). A tip end (16A) of an upstream side block (16) is formed in an acute angle and a material of a surface of the tip end (16A) is applied with treatment of any one of DLC, CrN, Hard Cr, and TiAlN, and a surface roughness Ra is set in a range of 1.3 to $5.0~\mu m$.

FIG.3



EP 2 564 939 A1

Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

10

20

30

35

50

55

[0001] The present invention relates to a coating apparatus and a coating method, and in particular to a coating apparatus and a coating method which can perform application of coating liquid stably when the coating liquid is applied by a bar coater while a web is being conveyed.

Description of the Related Art

[0002] A lithographic printing plate is generally manufactured by graining at least one face of a web made of pure aluminum or aluminum alloy, forming an anode oxide film on the at least one face, as necessary, to form a support web, then applying image recording layer coating liquid to the grained face, drying the same to form an image recording layer, and forming an overcoat layer on the image recording layer if necessary.

[0003] As such a coating apparatus for applying coating liquid, a bar coater is generally used. The bar coater includes a bar which contacts with a lower face of a continuously-running web and rotates. The bar coater forms a coating liquid reservoir portion by discharging coating liquid on an upstream side of the bar in a running direction of the web and applies the coating liquid on the lower face of the web.

[0004] Now, in a coating system where excessive liquid feeding is performed and metering is then performed, such as represented by a bar coating system, there exists a flow of liquid which separates into a required liquid amount and an excess liquid amount in a bead formation portion. In particular, in the bar coating system, a gas-liquid-solid interfaces exists at a weir (coating liquid reservoir portion) positioned on an upstream side of the bar. When drying of the coating liquid occurs at the region, the coating liquid is solidified and stacked, the drying affects bead formation and a streak failure is caused or a foreign material adhesion where a solidified material adheres to a coated surface is caused. Such a phenomenon easily occurs especially when the coating liquid has a high liquid viscosity (3mPa·s or more) and a high surface tension (30mN/m or more).

[0005] Incidentally, in Japanese Patent Application Laid-Open No. H08-266978, it is disclosed that a ceramic sintered compact such as Al_2O_3 is used as a material for a coating apparatus, and a ceramic coat layer having a center-line mean roughness Ra of 0.01 μ m to 1.00 μ m is provided on a liquid-contacting surface of the ceramic sintered compact so that the coating liquid is well prevented from soaking. In Japanese Patent Application Laid-Open No. H10-235256, it is disclosed that in a coating apparatus for a magnetic recording medium which applies a coating material on a band-like film while contacting with an outer face of a coating material outlet in a sliding manner, the outer face of the coating material outlet is coated with a diamond-like carbon (DLC) so as to prevent powder dropping. Further, in Japanese Patent Application Laid-Open No. H06-15214, it is disclosed that corrosion resistance is improved by coating a portion at which a coater dice contacts with a web and/or coating liquid with a film having a film hardness (Vickers hardness) of HV 1700 or more.

40 SUMMARY OF THE INVENTION

[0006] However, the coating apparatuses described in Japanese Patent Application Laid-Open Nos. H08-266978, H10-235256 and H06-15214 are different in object, coating system, and coating liquid from one another, and cannot prevent a streak failure or a foreign material adhesion from occurring due to drying of coating liquid.

[0007] In view of these circumstances, the present invention has been made, and an object thereof is to provide a coating apparatus and a coating method where, when a coating liquid is applied to a web while running in a bar coater, the solidification of the coating liquid can be prevented in a gas-liquid-solid interface of a weir positioned on an upstream side of a bar (coating liquid reservoir portion) so as not to cause a streak failure or a foreign material adhesion which is a failure caused by adhesion of the solidified material to a coated surface.

[0008] In order to solve the above problem, according to an aspect of the present invention, there is provided a coating apparatus including: at least a bar which contacts with a lower face of a web running continuously; a coating liquid supplying passage which supplies coating liquid on an upstream side of the bar to form a liquid reservoir portion; and an upstream side block which, on an upstream side of the liquid reservoir portion, forms another liquid reservoir portion of the coating liquid, wherein a tip end of the upstream side block is formed in an acute angle, a material of a surface of the tip end is subjected to treatment for any one of DLC, CrN, hard Cr, and TiAIN, and a surface roughness Ra of the tip end is in a range of 1.3 to 5.0 μm.

[0009] In the gas-liquid-solid interface of the weir positioned on the upstream side of the bar (the coating liquid reservoir portion), there is such a problem that the coating liquid becomes solidified to cause a streak failure or result in occurrence

of a foreign material adhesion where a solidified material adheres to a coated surface, but, since the tip end of the upstream side block is formed in an acute angle, the surface material of the upstream side block positioned at the tip end is subjected to a treatment for any one of DLC, CrN, hard Cr, and TiAlN, and the surface roughness Ra of the tip end of the upstream side block is set in a range of 1.3 to $5.0~\mu m$ in the present invention, wettability of the coating liquid to a material of the tip end of the upstream side block is improved so that such a phenomenon can be prevented that the coating liquid becomes solidified to cause a streak failure or result in a foreign material adhesion where a solidified material adheres to a coated surface. That is, a contacting angle of a surface of the material of the upstream side block at the tip end in a range from a moment when the liquid contacts with the surface of the tip and to 200 ms after the moment can be set to 65° or less, so that wettablity of the surface is improved.

[0010] Incidentally, when the surface roughness Ra of the tip end of the upstream side block is less than 1.3 μ m or more than 5.0 μ m, drying of the coating liquid occurs at the tip end of the upstream side block, so that a streak failure is easily caused.

[0011] In particular, DLC, CrN, hard Cr, or TiAlN is preferred in coating liquid containing water as a main solvent, and CrN, hard Cr, or TiAlN is preferred in liquid containing an organic solvent, for example, alcohol or ketones, as a main solvent. Here, the main solvent means a solvent which occupies 60% or more in all the solvents of the coating liquid.

[0012] Further, in the present invention, it is preferred that an upper end of the bar is disposed at a position higher than that of the tip end of the upstream side block.

[0013] Thereby, a scuff mark can be prevented from occurring due to contact of the web with the upstream side block.

[0014] Further, in the present invention, it is preferred that a clearance between the tip end of the upstream side block and the web is in a range of 0.2 mm to 1 mm.

[0015] By setting the clearance between the tip end of the upstream side block and the web to 1mm or less, application can be performed while forming fluid wall which blocks off accompanying air involved by running of the web, so that reliable coating can be performed without causing a failure such as a film breaking in the coated film.

[0016] By setting the clearance between the tip end of the upstream side block and the web to 0.2 mm or more to apply the coating liquid, it becomes hard to occur drying of the coating liquid at the tip end of the upstream side block so that it becomes hard to cause a streak failure.

[0017] In order to solve the above problem, the present invention provides a coating method which applies coating liquid using the above-described coating apparatus.

[0018] In the coating apparatus of the present invention, since the coating liquid is prevented from becoming solidified to cause a streak failure or result in occurrence of a foreign material adhesion where a solidified material adheres to a coated surface, an coated film which includes neither a streak failure nor a foreign material adhesion can be provided by applying coating liquid using the coating apparatus of the present invention.

[0019] Further, in the present invention, it is preferred that the coating liquid is applied to the web in a liquid-feeding amount per unit width of the web of 3 L/m·min. or more.

[0020] By setting the liquid-feeding amount of the coating liquid to 3L/m·min. or more, drying of the coating liquid hardly occurs at the tip end of the upstream side block, so that it becomes hard to cause a streak failure.

[0021] In the present invention, it is preferred that a liquid viscosity of the coating liquid is 3 mPa·s or more.

30

35

40

45

50

55

[0022] In the present invention, it is preferred that a surface tension of the coating liquid is 30 mN/m or more.

[0023] Since a streak failure or a foreign material adhesion occurs easily in coating liquid whose liquid viscosity is high (3 mPa·s or more) and whose surface tension is high (30 mN/m or more), it is notably effective to apply coating liquid using the coating apparatus of the present invention.

[0024] Incidentally, the application of the coating apparatus and the coating method according to the present invention is not limited to manufacturing of a lithographic printing plate, and the coating apparatus and the coating method according to the present invention can be used when application is performed using a bar in manufacture of a photosensitive material such as a photographic film, manufacture of a magnetic recording material such as a recording tape, manufacture of painted metal thin plate such as a colored iron plate, or the like. Therefore, as the web, flexible base materials which is formed in a continuous band shape and made of metal, plastic, paper, or the like, such as a lithographic printing plate precursor web obtained by forming a photosensitive or thermosensitive plate-making face on a grained face of a support web, a base material for a photographic film, a baryta paper for a developing paper, a base material for a recording tape, a base material for a video tape, a base material for floppy (registered trademark) disk, or the like are involved in addition to the support web described in the Description of the Related Art. Further, as the coating liquid, solution which is used to be applied to a web to be dried to form a film is involved, specifically, an overcoat layer forming liquid for protecting the photosensitive layer or the thermosensitive layer after formed is involved in addition to photosensitive layer forming liquid and thermosensitive forming liquid. Further, an intermediate layer forming liquid used to form an intermediate layer on a surface of a web to improve adhesion of a plate-making layer, photosensitive agent colloid liquid for a photosensitive film used to from a photosensitive layer for a photographic film, photosensitive agent colloid liquid for a developing paper used to form a photosensitive layer for a developing paper, a magnetic layer forming liquid used to form a magnetic layer for a recording tape, a video tape, or a floppy (registered trademark) disk, various paints used for painting a metal,

and the like are involved as the coating liquid.

[0025] According to the coating apparatus and the coating method according to the present invention, when coating liquid is applied to a web while the web is caused to run in a bar coater, the applied liquid is prevented from becoming solidified to cause a streak failure or result in occurrence of a foreign material adhesion where a solidified material adheres to a coated surface in a gas-liquid-solid interface of a weir (coating liquid reservoir portion) positioned on an upstream side of a bar.

BRIEF DESCRIPTION OF THE DRAWINGS

0 [0026]

15

20

30

35

40

45

50

55

Fig. 1 is a perspective view showing a configuration of an embodiment of a coating apparatus according to the present invention;

Fig. 2 is a sectional view of the coating apparatus shown in Fig. 1; and

Fig. 3 is an illustrative diagram showing a characteristic portion of the coating apparatus of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] Preferred embodiments of a coating apparatus and a coating method according to the present invention will be described below with reference to the drawings.

[0028] Fig. 1 and Fig. 2 show a configuration of an embodiment of a coating apparatus according to the present invention. Further, Fig. 3 shows a configuration of an applying section of the coating apparatus. As shown in Figs. 1 to 3, a coating apparatus 10 of a bar-coater type is an apparatus for performing application to a lower face of a running web, and is mainly composed of a bar 12, a bar supporting member 14, an upstream side block (also called "weir plate") 16, and a base 18. Incidentally, a web W is supported with path rollers 20 and 22, and runs in a direction of arrow "A". [0029] The bar 12 is formed in a cylindrical shape and is rotatably supported by the bar supporting member 14. The bar 12 is rotated about an axial line while contacting with a lower face of the running web W. It is preferred that a rotation direction of the bar 12 is a direction opposed to a running direction "A" of the web W and a peripheral velocity of the bar 12 is set within 1% of a running velocity of the web W. Incidentally, a rotation direction of the bar 12 may be the same as the running direction "A".

[0030] A surface of the bar 12 may be finished to be smooth, but may be provided with grooves disposed at a constant interval in a circumferential direction thereof, and it has a wire densely wound thereon. A diameter of the wire wound on the bar 12 is preferably in a range of 0.07 to 1 mm, more preferably 0.07 to 0.4 mm. In addition, regarding the bar provided with the grooves and the bar having the wire wound thereon, a coating thickness of a photosensitive layer forming liquid can be made thin by making the depth of the grooves and the thickness of the wire small, while the coating thickness of the photosensitive layer forming liquid can be made thick by making the depth of the grooves and the thickness of the wire large.

[0031] It is preferred that the diameter of the bar 12 is in a range of 6 to 25 mm because of manufacture thereof and such a range is further preferred because a vertical streak hardly occurs on an coated film of the photosensitive layer forming liquid formed on the web W. Further, the bar 12 is generally longer than the width of the web W, but may have the same length as the width of the web W.

[0032] The web W comes in contact with the bar 12 at a predetermined wrap angle in a state where the web W has been applied with tension. An entrance angle between the web W on an upstream side and a horizontal face is preferably in a range of 3° to 30°, more preferably in a range of 5° to 10°. By setting the entrance angle in this manner, thick coating at the start time of coating and at the ending time of coating can be prevented, and wear of the bar 12 can be suppressed. An angle (exit angle) between the web W on a downstream side and the horizontal face is not limited to a specific one, but the wrap angle is set such that the contact angle falls within a predetermined value.

[0033] The bar supporting member 14 is formed by assembling a plurality of blocks, and has an arc-shaped groove 14A on its upper face. The bar 12 engages with the groove 14A and is rotatably supported therein. An upstream side upper face 14B inclined with respect to a horizontal face is formed on an upstream side of the groove 14A in the running direction "A" of the web W (hereinafter, simply referred to as "upstream side").

[0034] A horizontal downstream side upper face 14C is formed on a downstream side of the groove 14A in the running direction "A" of the web W (hereinafter, simply referred to as "downstream side"). The downstream side upper face 14C is formed at a height position lower than the upstream side upper face 14B. A wall face 14D of the bar supporting member 14 on the upstream side is formed vertically, and an upstream side block 16 is disposed on the upstream side to face the wall face 14D.

[0035] The upstream side block 16 is a plate-like member provided vertically, and a lower end thereof is fixed to the base 18. Further, as shown in Fig. 3, an upper end (tip end) 16A of the upstream side block 16 is formed in an acute-angled

wedge shape. That is, a taper face 16B for forming a wedge shape whose vertical-sectional shape gradually becomes narrower toward the tip end 16A is formed on a face of the upstream side block 16 on the upstream side in the running direction of the web W.

[0036] Further, the tip end 16A of the upstream side block 16 is formed in a straight-line shape along the wide direction of the web W, and a parallel degree thereof is set in a range of 0.01 mm to 0.2 mm. Incidentally, the smaller the parallel degree becomes, the higher an effect described later becomes, but since working cost is increased as the parallel degree becomes smaller, the parallel degree is preferably 0.01 mm or more, more preferably 0.05 mm or more.

[0037] Accordingly, since the tip end 16A of the upstream side block 16 is formed in the acute-angled wedge shape and extends in a straight line along the width direction of the web W in this manner, a contact line where the web W first contacts with coating liquid is formed in a straight line along the width direction of the web W, and coating liquid passing through a clearance between the web W and the weir plate tip end 16A is pressurized (pressure is applied) in the contact line. Therefore, involved air on a surface of the web is effectively prevented from passing through the contact line to be brought into a coating liquid reservoir portion A. Thereby, even when a line velocity of the web W (a running velocity of the web) is increased for a high-speed coating, reliable coating can be performed without coating defect. Here, the angle of the tip end 16A is particularly preferably in a range of 5 to 45°. By setting the angle to 5° or more, machining accuracy is improved so that a high-precision block can be manufactured, and by setting the angel to 45° or less, stability of the above-described contact line is further improved.

10

20

30

35

40

45

50

55

[0038] However, a gas-liquid-solid interface exists in coating liquid which overflows toward the upstream side beyond the tip end 16A of the upstream side block 16 of such a coating apparatus 10, so that drying of coating liquid easily occurs at the tip end 16A of the upstream side block 16. When drying of coating liquid occurs at the tip end 16A of the upstream side block 16, the coating liquid becomes solidified and deposits. This affects bead formation, and a streak failure is caused or a foreign material adhesion where a solidified material adheres to a coated surface is caused. Such a phenomenon easily occurs especially in coating liquid having a high liquid viscosity (3mPa·s or more) and a high surface tension (30mN/m or more).

[0039] In view of these circumstances, a material of the surface of the tip end 16A of the upstream side block 16 is subject to a treatment for any one of DLC, CrN, hard Cr, and TiAlN, and a surface roughness Ra of the tip end 16A of the upstream side block 16 is set to fall within a range of 1.3 to 5.0 μm, so that a contact angle between a surface of the material of the tip end 16A of the upstream side block 16 and the coating liquid becomes 65° or less in a range from a moment when the coating liquid contacts to the surface of the tip end 16A of the upstream side block 16 to 200 ms after the moment. Whereby, an even overflow over a whole surface can be formed, and solidification of the coating liquid can be prevented so as no to cause a streak failure or a foreign material adhesion where the solidified material adheres to a coated surface.

[0040] When the surface roughness Ra of the tip end of the upstream side block is less than 1.3 or larger than 5.0, overflow breaking occurs at the tip end of the upstream side block and dry of the coating liquid occurs, which causes a streak failure easily.

[0041] Further, it is preferred that the surface roughness Ra of the tip end 16A of the upstream side block 16 is in a range of 1.3 to 5.0 μ m. When the surface roughness Ra of the tip end of the upstream side block is less than 1.3 or larger than 5.0, shortage of overflow occurs at the tip end of the upstream side block and the drying of the coating liquid occurs, which causes a streak failure easily.

[0042] Further, as shown in Fig. 3, it is preferred that, with reference to a parallel line 17 which passes through the tip end 16A of the upstream side block 16 and is parallel with the web W, a distance C1 from the web W to the parallel line 17 is 1 mm or less. In this case, when the distance C1 is excessively small, the web W contacts with the tip end 16A of the upstream side block 16 due to fine vibrations of the web W or the like, so that a scuff mark may occur. Therefore, it is preferred that the distance C1 is not less than 0.2 mm. Further, by performing application of coating liquid while setting the distance C1 to 0.2 mm or more, dry hardly occurs at the tip end of the upstream side block, so that a streak failure is hardly caused.

[0043] It is preferred that an upper end 12A of the bar 12 is disposed at a position higher than the tip end 16A of the upstream side block 16. That is, a difference H in height between the upper end 12A of the bar 12 and the tip end 16A of the upstream side block 16 is set to be positive. In other words, it is preferred that the position of the upper end 12A of the bar 12 is higher than the position of the tip end 16A of the upstream side block 16. By arranging the upper end 12A of the bar 12 at a position higher than the tip end 16A of the upstream side block 16, excessive coating liquid scrapped off from a coated film face by the bar 12 flows in a direction from the bar 12 to the upstream side block 16. Thereby, since the excess coating liquid flows in a direction opposite to a direction in which involved air is brought, bringing the involved air in the coating liquid reservoir portion A can be prevented further effectively.

[0044] Furthermore, the tip end 16A of the upstream side block 16 is disposed at a position higher than an upstream side upper end 14E of an upstream side upper face 14B of the bar supporting member 14. In other words, the tip end 16A of the upstream side block 16 is disposed at a position closer to the web W than the upstream side upper face 14B of the bar supporting member 14. Thereby, since pressure is easily applied to the coating liquid reservoir portion A

enclosed by the web W, the bar 12, the upstream side block 16, and the upstream side upper face 14B, high-speed coating can be performed so as not to cause coating defect.

[0045] The upstream side block 16 is provided to be parallel to the wall face 14D of the bar supporting member 14 so as to have a predetermined clearance between the upstream side block 16 and the wall face 14D, so that a slit-like supply flow passage 24 is formed between the upstream side block 16 and the wall face 14D. Incidentally, it is preferred that the supply flow passage 24 is narrow in view of such a point that a discharge pressure can be elevated without changing a supply amount of coating liquid (image recording layer coating liquid, overcoat layer coating liquid or the like), and it is preferred that the coating liquid is supplied such that a liquid-feeding amount per unit width of a web is 3L/m·min or more.

[0046] As shown in Fig. 1 and Fig. 2, the supply flow passage 24 is in communication with a temporary reservoir chamber 26 provided within the base 18. The temporary reservoir chamber 26 is connected to a discharge side of a pump P which supplies the coating liquid from a reservoir tank (not shown) for coating liquid, and coating liquid is supplied to the temporary reservoir chamber 26 by driving the pump P.

[0047] The temporary reservoir chamber 26 temporarily reserves coating liquid supplied and has a function of suppressing fluctuation of a flow rate of the coating liquid supplied from the supply flow passage 24 when a discharge rate of the pump P fluctuates. The coating liquid supplied to the temporary reservoir chamber 26 flows from a lower end of the supply flow passage 24 to an upper end thereof to be discharged from an outlet at the upper end toward a lower face of the web W. Thereby, the coating liquid reservoir portion A is formed in a space enclosed by the lower face of the web W, the upstream side upper face 14B of the bar supporting member 14, the bar 12 and the upstream side block 16. The coating liquid in the coating liquid reservoir portion A is caused to adhere to the surface of the web W so that application (coating) is performed.

[0048] As shown in Fig. 2, the base 18 is provided with an overflow liquid pool 28 on the upstream side of the upstream side block 16, and coating liquid which has overflowed beyond the tip end 16A of the upstream side block 16 to the upstream side can be received in the overflow liquid pool 28. Further, the base 18 is provided with an overflow liquid pool 30 on the downstream side of the bar supporting member 14, and coating liquid, which does not adhere to the web W and overflows to the downstream side, of the coating liquid in the coating liquid reservoir portion A can be received in the overflow liquid pool 30. Incidentally, it is preferred that the coating liquids received in the overflow liquid pools 28 and 30 are returned to the reservoir tank (not shown) through return pipes (not shown).

[0049] As shown in Fig. 1, side plates 32 and 34 are provided at both side edges of the base 18, so that side walls of the overflow liquid pools 28 and 30, the supply flow passage 24, and the temporary reservoir chamber 26 are formed. [0050] Incidentally, the above-described base 18 is supported by an elevating device (not shown) and can be moved in a height direction (vertical direction). Therefore, the bar 12 can be advanced toward the web W (namely, upward direction) to be caused to contact with the web W and can be retracted from the web W (namely, moved downward) to be separated from the web W. Incidentally, a running position of the web W can be changed by ascending or descending the path rollers 20 and 22 instead of movement of the base 18.

[0051] Incidentally, in this embodiment, the coating apparatus 10 including a weir (coating liquid reservoir portion) only on the upstream side has been described, but same holds true for a coating apparatus where a weir is also provided on the downstream side in addition to the upstream side. In the coating apparatus where a weir is also provided on the downstream side in addition to the upstream side, it is preferred that as a material of the tip end of the downstream side block, a material which enables to make a contact angle 65° or less in a range from a moment when the coating liquid contacts to the surface of the tip end of the downstream side block till 200 ms after the moment, is also used.

[Application of image recording layer to lithographic printing plate aluminum web and application of overcoat layer to image recording layer]

[0052] A lithographic printing plate precursor is obtained by applying an image recording layer on an aluminum support which has been subjected to surface roughing treatment and then anode oxidation treatment. An undercoat may be applied between the aluminum supporting layer and the image recording layer, or an overcoat layer may be applied to the image recording layer if needed.

[0053] Main solvents of coating liquids of the image recording layer and the undercoat are organic solvents, where alcohol solvent or ketone solvent is preferably used. As the alcohol solvent, methanol, ethanol, propanol, 1-methoxy-2-propanol, and the like are preferably used, while as the ketone solvent, acetone, methyl ethyl ketone, and the like are preferably used. Main solvent of coating liquid of the overcoat layer is water. Examples

<Contact angle measuring method of base plate>

10

20

30

35

40

45

50

55

[0054] A contact angle of coating liquid at a moment of liquid adhesion was measured using a surface force apparatus DM700 (trademark) manufactured by KYOWA INTERFACE SCIENCE CO., LTD. However, as the contact angle of liquid

at a moment when the coating liquid contacts with the tip end of the block, was unstable due to vibrations of liquid droplet, so that wettability of a substrate was evaluated at a contact angle when 200 ms after the moment when the coating liquid contacts to the surface of the tip end.

[0055] Measurement conditions were as follows:

5

10

- · Environment: room temperature of 25°C and moisture of 30 to 50%
- · Liquid droplet formation condition: time of 2300 ms/voltage of 1000 mV

[0056] As measurement data, an average value of 5 times was adopted. Incidentally, As coating liquid, the following liquids were used. Measurement results are shown in TABLE 1.

(Overcoat layer coating liquid (1))

[0057]

15

- · Mica-dispersed liquid (1) described below: 8.0g
- · Polyvinyl alcohol (saponification degree: 98.5 mol%)

(PVA110 (trademark) produced by KURARAY CO., LTD.): 1.3g

· Water: 133g

20

25

30

(Preparation of mica-dispersed liquid (1))

[0058] Mica-dispersed liquid (1) was obtained by adding synthetic mica ("somasif ME-100 (trademark)" produced by Co-op Chemical Co., Ltd. and Aspect ratio: 1000 or more) of 32g in water of 368g, and dispersing the synthetic mica such that an average particle diameter (measured by a laser light scattering method) reached 0.5 µm using a homogenizer.

<Measurement of roughness of base plate>

[0059] Roughness of a base plate could be measured by using a general roughness gauge, but roughness was measured by using SURFCOM 1400 (trademark) manufactured by TOKYO SEIMITSU CO., LTD in this patent application. Measurement conditions were as follows:

- · Measurement conditions: velocity: 1.5 mm/s, and measurement length: 20mm
- · Sensing pin: tip end: 2µmR

35

Measurement results are shown in TABLE 1

[0060]

45

40

50

55

TABLE 1

Material (Ra)	Contact Angle (at 200 ms)
DCL (0.01)	50
Tin (0.01)	70
CrN (0.01)	45
TiAIN (0.01)	30
Hard Cr (0.01)	30
SUS304 (0.01)	65

(Experiment 1)

[Manufacture of Web before application]

[0061] In order to remove rolling oil on a surface of an aluminum plate (Material: JIS (Japanese Industrial Standards) A 1050) having a thickness of 0.3 mm, degreasing treatment was performed using sodium aliminate aqueous solution

of 10 mass% at a temperature of 50°C for 30 seconds. Thereafter, a surface of the aluminum plate was sand-grained using three nylon brushes having a bundle of bristles with a bristle diameter of 0.3 mm and suspension of water and pumice with a medium size of 25 µm (specific gravity: 1.1 g/cm³), and the aluminum plate was well cleaned. The aluminum plate was dipped in aqueous sodium hydroxide of 25 mass% at a temperature of 45°C for 9 seconds, and etching was performed. After washed with water, the aluminum plate was dipped in nitric acid of 20 mass% at a temperature of 60°C for 20 seconds and was washed with water. The etching amount of the sand-grained surface at this time was about 3 g/m². [0062] Next, an electro-chemical surface roughing treatment was continuously performed using AC voltage with a frequency of 60Hz. Electrolytic solution used at this time was aqueous solution of nitric acid of 1 mass% (containing aluminum ions of 0.5 mass%) at a liquid temperature of 50°C. Using a waveform of the AC voltage source as a trapezoidal rectangular wave AC waveform where a time TP where a current value from zero to a peak was 0.8 msec and a duty ratio was 1:1, the electro-chemical surface roughing treatment was performed utilizing a carbon electrode as an opposite electrode. Ferrite was used as an auxiliary anode. A current density was 30A/dm² at a peak value of current, and 5% of current flowing from a power source to the auxiliary anode was shunted. An electric amount in nitric acid electrolysis was 175C/dm² which was an electric amount at an anode time of the aluminum plate. The aluminum plate was washed with water by spraying.

[0063] Subsequently, an electro-chemical surface roughing treatment was performed in a method similar to the nitric acid electrolysis in electrolytic solution of aqueous solution of hydrochloric acid of 0.5 mass% (containing aluminum ions of 0.5 mass%) at a liquid temperature of 50°C under such a condition that an electric amount at an anode time of the aluminum plate was 50C/dm², and thereafter, the aluminum plate was washed with water by spraying.

[0064] Next, after a DC current anode oxide film of 2.5 g/m² was provided on the aluminum plate at a current density of 15A/dm² using sulfuric acid of 15 mass% (containing aluminum ions of 0.5 mass%) as electrolytic solution, the aluminum plate was washed with water and dried.

[0065] Thereafter, in order to secure hydrophilia of a non-image portion, silicate treatment was performed to the aluminum plate using No. 3 sodium silicate aqueous solution of 2.5 mass% at a temperature of 60° C for 10 seconds and thereafter the aluminum plate was washed with water to obtain a band-like support. Here, No. 3 sodium silicate aqueous solution means Di Sodium Tri Silicate aqueous solution (Na₂O-3SiO₂) having mole ratio of three, which is specified by JIS K1408 (JIS: Japanese Industrial Standards). The deposit amount of Si was 10 mg/m². A center-line mean roughness of the base plate which was measured using a needle having a diameter of 2 μ m was 0.51 μ m.

[Application of undercoat]

[0066] Next, after the coating liquid for a undercoat was applied to the above band-like support 12 such that a dried application amount was 20mg/m², dry was performed at a temperature of 80°C for 10 seconds using a hot air dryer to produce a band-like support 12 having the undercoat to be used for experiment described below.

<Coating liquid for an undercoat>

[0067]

10

15

20

25

30

35

40

45

50

55

· compound for a undercoat having a structure described below (1):	0.18 g
· hydroxyethyl iminodiacetic acid:	0.10 g
· ethanol	55.24 g
· water	6.15 g

Compound for an undercoat (1)

[Application and dry of image recording layer]

[0068] After coating liquid for an image recording layer having the composition described below was applied to the undercoat formed in the above manner by an application machine for an image recording layer, the coating liquid was

dried by a dryer for an image recording layer. An application amount of the image recording layer was set to 1.0 g/m² after dried.

[0069] The coating liquid for an image recording layer was obtained by mixing and stirring photosensitive liquid (1) described below and micro-gel liquid (1) immediately before applied.

<Photosensitive liquid (1)>

[0070]

5

10	· binder polymer (1) [structure described below]:	0.240 g
	· infrared absorbing dye (1) [structure described below]:	0.030 g
	· radical polymerization initiator (1) [structure described below]:	0.162 g
	· radical polymerizable compound tris(acryloyl oxyethyl)isocyanurate (NK Ester A produced by Shin-Nakamura Chemical Co., Ltd.):	0.192 g
15	· low-molecular hydrophilic compound tris(2-hydroxyethyl)isocyanurate:	0.062 g
	· low-molecular hydrophilic compound (1) [structure described below]:	0.050g
	· polymer containing ammonium group [structure described below]: [reduction ratio viscosity: 44cSt/g/ml]	0.035 g
	· fluorochemical surfactant (1) [structure described below]:	0.008 g
20	· 2-butanone:	1.091 g
	· 1-methoxy-2-propanol:	8.609 g

<microgel liquid (1)>

[0071]

25

30

35

40

45

50

· microgel (1): 2.640 g · distilled water: 2.425 g

[0072] Structures of the above-described binder polymer (1), radical polymerization initiator (1), infrared absorbing dye (1), low-molecular hydrophilic compound (1), fluorochemical surfactant (1), and polymer containing ammonium group, and a synthesis method of the microgel (1) are as follows:

binder polymer (1);

infrared absorbing dye (1);

radical polymerization initiator (1);

$$\begin{array}{c} -(-CH_{2}CH_{-})_{30} \\ -(-CH_{2}CH_{-})_{30} \\ -(-CH_{2}CH_{-})_{70} \\ -(-CH_{2}CH_{-})_{70} \\ -(-CH_{2}CH_{-})_{11} -(-CC_{3}H_{6})_{22} -(-CC_{2}H_{4})_{11} -OH \\ -(-CH_{2}CH_{-})_{11} -(-CH_{2}CH_{-})_{11} -OH \\ -(-CH_{2}CH_{-})_{70} \\$$

low-molecular hydrophilic compound (1);

polymer containing ammonium group

-Synthesis of microgel (1)-

5

10

15

20

25

30

35

40

45

50

55

[0073] As oil-phase components, adduct of trimethylolpropane and Xylylene Diisocyanate (TAKENATE D-110N (trademark) produced by Mitsui Chemical Polyurethane Co., Ltd) of 10g, pentaerythritol acrylate (SR444 produced by Nippon Kayaku Co., Ltd.) of 3.15g and PIONIN A-41C (trademark) (produced by TAKEMOTO OIL & FAT Co., Ltd.) of 0.1g were dissolved in ethyl acetate of 17g. As a water-phase component, aqueous solution with PVA-205 (trademark) of 4 mass% of 40g was prepared. The oil-phase components and the water-phase component were mixed and emulsified for 10 minutes at 12,000rpm using a homogenizer. After the emulsified material obtained was added to distilled water of 25g and stirred at a room temperature for 30 minutes, the emulsified material was further stirred at a temperature of 50°C for 3 hours. The microgel thus obtained was diluted using distilled water such that a concentration of a solid component of the microgel became 15 mass%, which resulted in the microgel (1). When an average particle diameter of the microgel was measured by a light scattering method, the average particle diameter was 0.2 μm.

[Application of overcoat layer coating liquid]

[0074] The above-described overcoat layer coating liquid (1) (viscosity: 3mPa·s and surface tension: 35 mN/m) was applied to a web W applied with tension of 100 kg/m at a rate (line speed or web speed) of 50 m/min in an application amount of $10cc/m^2$ while the bar 12 was rotated at a rotation speed of 5rmp in a direction opposite to the running direction "A" of the produced web W before applied using a wedge-shaped block where the angle of the upstream side block 16 was an acute angle of 30° in the bar coater 10 shown in Fig. 1 and Fig. 2. As the application conditions, it was adopted that the clearance between the web and the tip end of the upstream side block was 0.2 mm and the liquid feeding amount was 3L/m·min. While the material of the upstream side block (weir) and the surface roughness were changed, dries of

coating liquid at the upstream side block and coating defects were confirmed. The test result was shown in TABLE 2. **[0075]** Incidentally, the viscosity and the surface tension of the coating liquid was measured by the following measuring method.

5 <Liquid viscosity measuring method>

10

20

30

35

40

45

50

55

[0076] The viscosity was measured using B-type viscometer (TVB-10) (trademark) manufactured by TOKI SANGYO CO., LTD.

[0077] The measurement conditions were as follows:

· Environment: room temperature of 25°C and moisture of 30 to 50%

[0078] An average value of three times was adopted as measured data.

15 <Surface tension measuring method>

[0079] The surface tension was measured by using DY300 (trademark) manufactured by KYOWA INTERFACE SCIENCE CO., LTD.

[0080] The measurement conditions were as follows:

· Environment: room temperature of 25°C and moisture of 30 to 50%

[0081] An average value of three times was adopted as measured data.

25 TABLE 2

		TABLE 2		
Level	Weir material/Contact angle (200ms unit °)	Roughness Ra (μm)	Dry of weir	Condition of coated face
Test 1-1	DCL/50	1	Presence	Streak
Test 1-2	DCL/50	1.3	Absence	Good
Test 1-3	DCL/50	3	Absence	Good
Test 1-4	DCL/50	5	Absence	Good
Test 1-5	DCL/50	5.5	Presence	Streak
Test 1-6	DCL/70	3	Presence	Streak
Test 1-7	DCL/70	5	Presence	Streak
Test 1-8	CrN/45	1	Presence	Streak
Test 1-9	CrN/45	1.3	Absence	Good
Test 1-10	CrN/45	5	Absence	Good
Test 1-11	CrN/45	5.5	Presence	Streak
Test 1-12	SUS304/65	1.3	Presence	Streak
Test 1-13	SUS304/65	3	Absence	Good
Test 1-14	SUS304/65	5	Absence	Good
Test 1-15	TiAIN/30	1	Presence	Streak
Test 1-16	TiAIN/30	1.3	Absence	Good
Test 1-17	TiAIN/30	5	Absence	Good
Test 1-18	TiAIN/30	5.5	Presence	Streak
Test 1-19	Hard Cr/30	1	Presence	Streak
Test 1-20	Hard Cr/30	1.3	Absence	Good
Test 1-21	Hard Cr/30	5	Absence	Good

(continued)

Level	Weir material/Contact angle (200ms unit °)	Roughness Ra (μm)	Dry of weir	Condition of coated face
Test 1-22	Hard Cr/30	5.5	Presence	Streak

(Experiment 2)

5

10

15

20

25

30

35

40

45

50

55

[0082] With the weir material of the above-described Test 1-2, the clearance between the web and the upstream side block (weir) and the liquid-feeding amount were changed. The test results were shown in TABLE 3.

TABLE 3

Level	Liquid feeding amount (L/m·min.)	Clearance (mm)	Dry of weir	Condition of coated face
Test 2-1	3	0.1	Presence (×)	Streak
Test 2-2	3	0.2	Absence (O)	Good
Test 2-3	3	0.3	Absence (O)	Good
Test 2-4	4	0.1	Presence (×)	Streak
Test 2-5	4	0.2	Absence (O)	Good
Test 2-6	4	0.3	Absence (O)	Good
Test 2-7	5	0.1	Presence (O)	Streak
Test 2-8	5	0.2	Absence (O)	Good
Test 2-9	5	0.3	Absence (O)	Good
Test 2-10	6	0.1	Absence (O)	Good
Test 2-11	6	0.2	Absence (O)	Good
Test 2-12	6	0.3	Absence (O)	Good
Test 2-13	2	0.1	Presence (×)	Streak
Test 2-14	2	0.2	Presence (×)	Streak
Test 2-15	2	0.3	Absence (O)	Good
Test 2-16	3	0.8	Absence (O)	Good
Test 2-17	3	1.0	Absence (O)	Good
Test 2-18	3	1.2	Absence (O)	Coating impossible

(Experiment 3)

[Manufacture of Web before application]

[0083] In order to remove rolling oil on a surface of an aluminum plate (Material: JIS (Japanese Industrial Standards) A 1050) having a thickness of 0.3 mm, degreasing treatment was performed using sodium aliminate aqueous solution of 10 mass% at a temperature of 50° C for 30 seconds. Thereafter, a surface of the aluminum plate was sand-grained using three nylon brushes having a bundle of bristles with a bristle diameter of 0.3 mm and suspension of water and pumice with a medium size of 25 μ m (specific gravity: 1.1 g/cm³), and the aluminum plate was well cleaned with water. The aluminum plate was dipped in aqueous sodium hydroxide of 25 mass% at a temperature of 45°C for 9 seconds, and etching was performed. After washed with water, the aluminum plate was dipped in nitric acid of 20 mass% at a temperature of 60°C for 20 seconds and was washed with water. The etching amount of the sand-grained surface at this time was about 3 g/m².

[0084] Next, an electro-chemical surface roughing treatment was continuously performed using AC voltage with a frequency of 60Hz. Electrolytic solution used at this time was aqueous solution of nitric acid of 1 mass% (containing aluminum ions of 0.5 mass%) at a liquid temperature of 50°C. Using a waveform of the AC voltage source as a trapezoidal

rectangular wave AC waveform where a time TP where a current value from zero to a peak was 0.8 msec and a duty ratio was 1:1, the electro-chemical surface roughing treatment was performed utilizing a carbon electrode as an opposite electrode. Ferrite was used as an auxiliary anode. A current density was 30A/dm² at a peak value of current, and 5% of current flowing from a power source to the auxiliary anode was shunted. An electric amount in nitric acid electrolysis was 175C/dm² which was an electric amount at an anode time of the aluminum plate. The aluminum plate was washed with water by spraying.

[0085] Subsequently, an electro-chemical surface roughing treatment was performed to the aluminum plate in a method similar to the nitric acid electrolysis in electrolytic solution of aqueous solution of hydrochloric acid of 0.5 mass% (containing aluminum ions of 0.5 mass%) at a liquid temperature of 50°C under such a condition that an electric amount at an anode time of the aluminum plate was 50C/dm², and thereafter, the aluminum plate was washed with water by spraying.

[0086] Next, after a DC current anode oxide film of 2.5 g/m² was provided on the aluminum plate at a current density of 15A/dm² using sulfuric acid of 15 mass% (containing aluminum ions of 0.5 mass%) as electrolytic solution, the aluminum plate was washed with water and dried.

[0087] Thereafter, in order to secure hydrophilia of a non-image portion, silicate treatment was performed to the aluminum plate using sodium silicate aqueous solution No. 3 of 2.5 mass% at a temperature of 60°C for 10 seconds and thereafter the aluminum plate was washed with water to obtain a band-like support. The deposit amount of Si was 10 mg/m^2 . A center-line mean roughness of the base plate which was measured using a needle having a diameter of 2 μ m was 0.51 μ m.

20 [Application of coating liquid for image recording layer]

50

55

[0088] Using the bar coater shown in Fig. 1 and Fig. 2, the coating liquid described below (viscosity: 10mPa·s and surface tension: 25mN/m) was applied to the web W applied with tension of 100 kg/m in an application amount (coating amount) of 10 cc/m² while the bar 12 was being rotated at a speed of 5rpm in a direction opposite to the running direction "A" of the web W. As the application conditions, it was adopted that the clearance between the web and the tip end of the upstream side block was 0.2 mm and the liquid feeding amount was 3L/m·min. While the material of the upstream side block (weir) and the surface roughness were changed, dries of coating liquid at the upstream side block and coating defects were confirmed. The test result was shown in TABLE 4.

30	· binder -1: · diazo resin - 1:	5.0g 2.5g
	· oil-soluble dye (Victoria Pure blue BOH):	0.15g
	· fluorochemical surfactant (Megafack F-177 (trademark) produced by DIC CORPORATION)	
25	· tricresyl phosphate:	0.2g
35	· phosphorous acid:	0.03g
	· maleic acid:	0.03g
	· half ester according to n-Hexyl alcoholof styrene-maleic anhydride copolymer:	0.05g
	Solvent	
40	· 2-hydroxy-2-methyl methyl propanoate:	20.00g
	· 1-methoxy-2-propanol:	20.00g
	· methyl lactate:	7.00g
	· methanol:	25.00g
45	· methyl ethyl ketone:	25.00g
45	· water:	3.00g

[0089] The diazo resin -1 is hexafluorophosphate of condensation product of p-diazodiphenylamine with paraformal-dehyde, which is described in Synthesis Example - 1 in Japanese Patent Application Laid-Open No. S59-78340. The binder - 1 is water-insoluble and alkaline water-soluble film-forming polymer of 2-hydroxyethyl methacrylate/acrylonitrile/methyl methacrylate/methacrylic acid copolymer (weight ratio: 50/20/26/4, average molecular weight: 75,000, and acid content: 0.4meq/g).

TABLE 4

Level	Weir material	Roughness Ra (μm)	Drying of weir	Condition of coated face
Test 3-1	TiN	3	Presence	Streak

(continued)

Level	Weir material	Roughness Ra (μm)	Drying of weir	Condition of coated face
Test 3-2	TiN	5	Presence	Streak
Test 3-3	CrN	1	Presence	Streak
Test 3-4	CrN	1.3	Absence	Good
Test 3-5	CrN	5	Absence	Good
Test 3-6	CrN	5.5	Presence	Streak
Test 3-7	SUS304	1.3	Presence	Streak
Test 3-8	SUS304	3	Absence	Good
Test 3-9	SUS304	5	Absence	Good
Test 3-10	TiAIN	1	Presence	Streak
Test 3-11	TiAIN	1.3	Absence	Good
Test 3-12	TiAIN	5	Absence	Good
Test 3-13	TiAIN	5.5	Presence	Streak
Test 3-14	Hard Cr	1	Presence	Streak
Test 3-15	Hard Cr	1.3	Absence	Good
Test 3-16	Hard Cr	5	Absence	Good
Test 3-17	Hard Cr	5.5	Presence	Streak

(Conclusion of Experiment Result)

[0090] From TABLE 2 and TABLE 4, it is understood that by applying any one of treatment of DLC, CrN, Hard Cr, and TiAlN to the material of the surface of the tip end 16A of the upstream side block 16 and setting the surface roughness Ra of the tip end 16A of the upstream side block 16 in a range of 1.3 to 5.0 μm, the tip end of the upstream side block is prevented from drying, so that excellent application can be performed.

[0091] From TABLE 3, it is understood that it is preferred that the coating liquid is applied in such a condition that the liquid-feeding amount per unit width of web is 3L/m·min or more. Further, it is also understood that it is preferred that the coating liquid is applied in such a condition that the clearance between the tip end of the upstream side block and the web is 0.2 mm or more. When the clearance is more than 1 mm, application becomes impossible so that such a clearance cannot be adopted.

Claims

5

10

15

20

25

35

40

45

- 1. A coating apparatus at least comprising:
- a bar (12) which contacts with a lower face of a web (W) running continuously;
 - a coating liquid supplying passage (24) which supplies a coating liquid on an upstream side of the bar (12) to form a liquid reservoir portion; and
 - an upstream side block (16) which, on an upstream side of the liquid reservoir portion, forms another liquid reservoir portion of the coating liquid, wherein
 - a tip end (16A) of the upstream side block (16) is formed in an acute angle,
 - a material of a surface of the tip end (16A) is subjected to treatment for any one of DLC, CrN, hard Cr, and TiAIN, and
 - a surface roughness Ra of the tip end (16A) is in a range of 1.3 to 5.0 μm .
- The coating apparatus according to claim 1, wherein an upper end (12A) of the bar (12) is disposed at a position higher than the tip end (16A) of the upstream side block (16).
 - 3. The coating apparatus according to claim 1 or 2, wherein a clearance between the tip end (16A) of the upstream

side block (16) and the web (W) is in a range of 0.2 mm to 1 mm.

- **4.** A coating method for applying the coating liquid to the web (W) using the coating apparatus according to any one of claims 1 to 3.
- **5.** The coating method according to claim 4, wherein application of the coating liquid is performed such that a liquid-feeding amount per unit width of the web (W) is 3L/m·min or more.
- 6. The coating method according to claim 4 or 5, wherein a liquid viscosity of the coating liquid is 3mPa·s or more.
- 7. The coating method according to any one of claims 4 to 6, wherein a surface tension of the coating liquid is 30mN/m or more.
- **8.** The coating method according to any one of claims 4 to 7, wherein the web (W) is an aluminum web which has been subjected to a surface roughing treatment and has been further subjected to an anode oxide treatment.
- **9.** The coating method according to any one of claims 4 to 7, wherein the web (W) is an aluminum web which has been subjected to a surface roughing treatment and has been further subjected to an anode oxide treatment, and which has an image recording layer for a lithographic printing plate precursor.

20

15

5

10

25

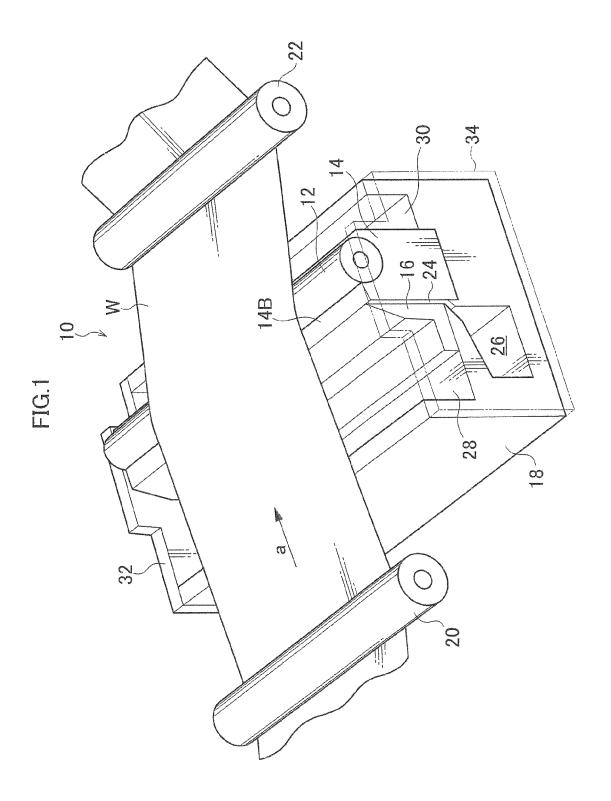
30

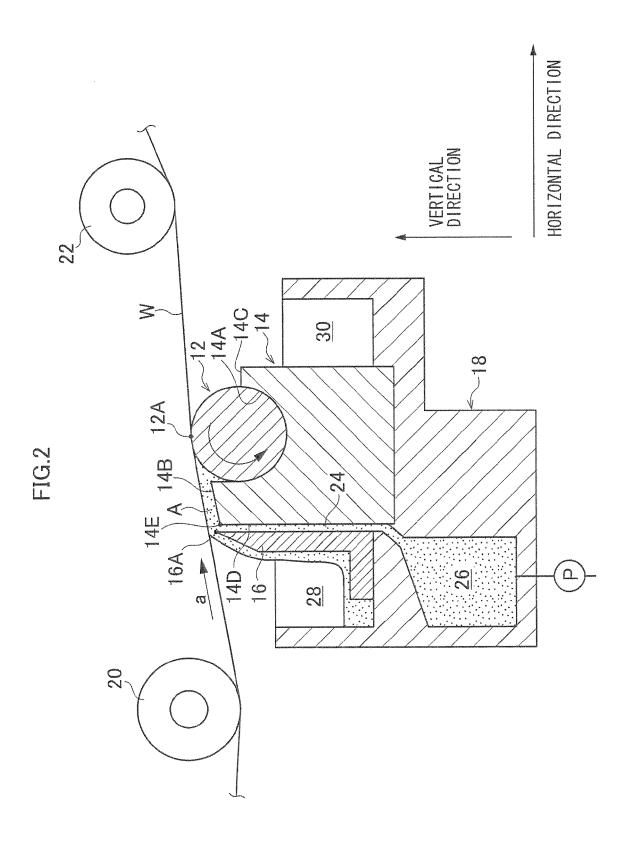
35

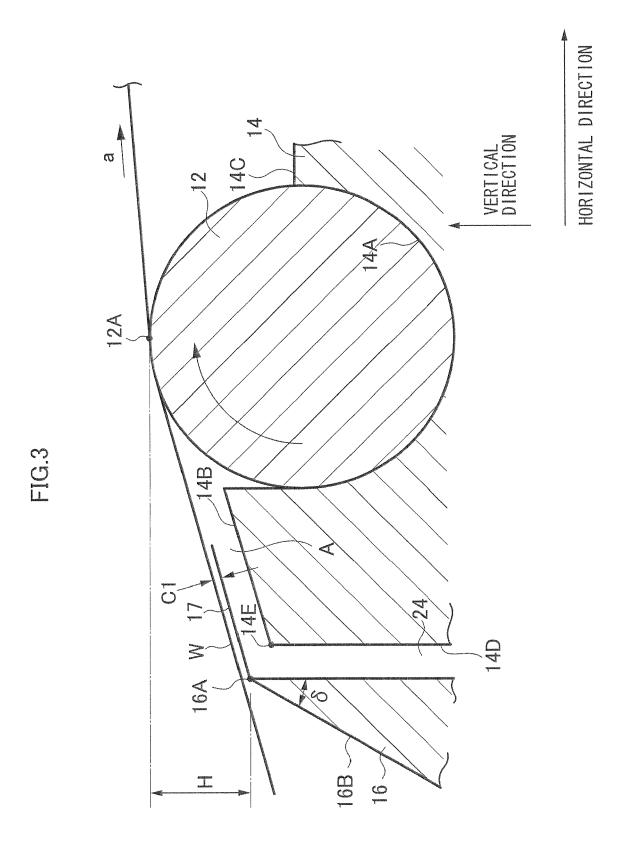
40

45

50









EUROPEAN SEARCH REPORT

Application Number EP 12 18 1701

	DOCUMENTS CONSID	ERED TO BE RELEVANT		
Category	Citation of document with ir of relevant pass	ndication, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Α	[JP]) 2 April 2003	JI PHOTO FILM CO LTD (2003-04-02) , [0229]; figures *	1	INV. B05C3/18 B05C5/02 B05C11/02
A	EP 1 342 508 A1 (FU [JP] FUJIFILM CORP 10 September 2003 (* paragraph [0037];	2003-09-10)	1	B03C11/02
A	JP 2003 275642 A (F 30 September 2003 (* abstract; figures		1	
A	JP 2003 236439 A (F 26 August 2003 (200 * abstract; figures		1	
Α	EP 1 872 861 A2 (FU 2 January 2008 (200 * figures *	JJFILM CORP [JP]) 8-01-02)	1	
A	EP 1 872 860 A1 (FU 2 January 2008 (200 * figures *	JIFILM CORP [JP]) 8-01-02)	1	TECHNICAL FIELDS SEARCHED (IPC)
Α	US 4 521 459 A (TAK 4 June 1985 (1985-6 * column 3, line 59 figures *	EDA HIDEO [JP]) 16-04) 1 - column 4, line 4;	1	
	The present search report has	oeen drawn up for all claims	-	
	Place of search	Date of completion of the search	1	Examiner
	Munich	25 January 2013	End	drizzi, Silvio
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document Coument of the same patent family, corresponding document				

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 12 18 1701

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

25-01-2013

	Patent document ed in search report		Publication date		Patent family member(s)		Publication date
EP	1297900	A2	02-04-2003	CN EP EP US	1408483 1297900 1803502 2004043154	A2	09-04-2003 02-04-2003 04-07-2007 04-03-2004
EP	1342508	A1	10-09-2003	AT CN EP JP US	422971 1442237 1342508 2003251256 2003170391	A1 A	15-03-2009 17-09-2003 10-09-2003 09-09-2003 11-09-2003
JP	2003275642	Α	30-09-2003	NONE	·		
JP	2003236439	Α	26-08-2003	NONE	:		
EP	1872861	A2	02-01-2008	CN EP JP US	101096024 1872861 2008264757 2008000421	A2 A	02-01-2008 02-01-2008 06-11-2008 03-01-2008
EP	1872860	A1	02-01-2008	CN EP JP US	101096025 1872860 2008006378 2008000418	A1 A	02-01-2008 02-01-2008 17-01-2008 03-01-2008
US	4521459	Α	04-06-1985	JP JP US	3061508 58223459 4521459	Α	20-09-1991 26-12-1983 04-06-1985

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP H08266978 B [0005] [0006]
- JP H10235256 B [0005] [0006]

- JP H0615214 B [0005] [0006]
- JP S5978340 B **[0089]**