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(54) **METHOD OF AND DEVICE FOR APPLICATION.**

(57) A hopper type application device for applying one or more coating liquids on a running flexible support member, wherein said device comprises a slit characterized by applying a composite plating film, in which fluorine-containing resin is dispersed and coagulated, to a lip portion disposed at the forward end and/or an inclined surface portion continuing to the lip portion, and a method of application, wherein the length of a bottom portion of a bead is made to be substantially equal to the length of lip at the inlet side when the plating is applied only to the inclined surface portion continuing to the lip portion, are used to thereby achieve the following object. There are provided the device for application, wherein troubles such as tailing, liquid dripping and waviness can be eliminated even when coating is performed by a slide hopper and an extrusion type coating die, with a liquid low in surface tension and viscosity used as a coating liquid, and the method of application capable of offering uniform coating properties.

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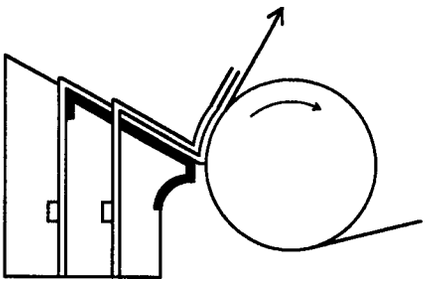
FIG. 2 (a)



FIELD OF THE INVENTION

The present invention relates to a coating apparatus of a hopper type, and more specifically, to a coating apparatus capable of offering excellent uniform coatability even for a coating solution having low surface tension and low viscosity.

BACKGROUND OF THE INVENTION

Coating apparatus of a slide hopper type and those of an extrusion hopper type are capable of performing high-speed coating, thin-layer coating and simultaneous multilayer coating, and some of them are used widely for photographic light-sensitive materials and others are used for magnetic recording materials widely, depending on their features. On coating apparatus of this type, a staying coating solution which is called a bead of a coating solution is formed between a coater tip (also called an edge or a lip) and a running flexible support (also called a web), and coating is performed through the bead.

On such a bead coater, stability of coating is extremely influenced by stability of the bead. The stability of the bead is influenced by factors including the distance setting up between a lip and a web, environmental conditions and physical properties of a coating solution, namely viscosity and surface tension. In the case of simultaneous multilayer coating, in particular, the relation of physical properties between layers greatly affects the bead stability, and when the coating speed is high, or when a coated layer is thin, it is difficult to secure the bead stability. In the case of an unstable bead, coating defects are caused such as pencil lines, streak defects and coating solution shortage.

For an improvement of such bead stability, there is known, for example, a method to provide a pressure difference between the upper portion and the lower portion of a bead. To be concrete, there has been taken a measure wherein a decompressed chamber is positioned below a bead to attract the bead downward, and thereby to improve the bead stability.

However, in the case of a coating solution having extremely low viscosity, for example, a coating solution having a viscosity of 10 cps or less, containing an organic solvent and having low surface tension, there have been some occasions wherein the coating solution oozes out of a lip portion other than the bead, and drips on a coated layer or on a support despite the above-mentioned measure, causing comet defects and dropping defects, or causing more streak defects even when the coating speed is not so high and a coated layer is not so thin.

For the problems mentioned above, it is suggested in Japanese Patent Publication No. 57629/1989 that a lip portion on the tip of a coating apparatus is provided with water-repellent resins. However, even when fluorine-containing resins are provided on the lip portion and the surface thereof is ground, for example, it is difficult to obtain satisfactory accuracy and strength on the lip portion due to the strength of the resins because the lip portion is required to have an extremely high accuracy. Therefore, it is difficult to obtain accuracy for a uniform coating layer thickness and scratches are easily caused, thus, it is difficult to maintain stable coating conditions.

OBJECT OF THE INVENTION

To overcome the problems mentioned above, the object of the invention is to provide a coating apparatus of a hopper type equipped with a dimensionally accurate lip which causes no coating defects including streak defects and is hardly scratched even in the case of coating with a coating solution having low surface tension and viscosity.

DISCLOSURE OF THE INVENTION

The object of the invention mentioned above can be achieved by both of a coating apparatus of a hopper type for coating one or more kinds of coating solutions on a running flexible support provided with a slit wherein a lip portion at the tip of a hopper and/or an inclined surface following the lip portion are subjected to composite plating to be covered by a coat of plating in which fluorine-containing resins are dispersed in a form of eutectoid, and of a method of coating under the condition that a length of the lower portion of a bead is equal to that of a part of the lip positioned at an upstream side when only the inclined surface following the lip portion is subjected to the composite plating.

Incidentally, it is preferable that the aforementioned coat of plating wherein fluorine-containing resins are made in a form of eutectoid is one plated with nickel through non-electrolytic plating utilizing a chemical reaction, and it is preferable that the coat of plating is subjected to heat treatment at a temperature of not

less than 300 ° C.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1(a) Explanatory sectional view showing oozed out solution on an extrusion coating die

Fig. 1(b) Explanatory plan view show oozed out solution on a coater of an extrusion hopper type

Fig. 2(a) Sectional view of a coater of a slide hopper type

Fig. 2(b) Sectional view of a coater of an extrusion hopper type

Fig. 2(c) Sectional view of a curtain coater (of a slide hopper type)

Fig. 2(d) Sectional view of a curtain coater (of an extrusion type)

Fig. 2(e) and Fig. 2(f) illustrations showing the relation between a length of a lower portion of a bead and that of a lip at an upstream side.

A detailed description of the invention will be given as follows.

The inventors of the present invention recognized the difficulty of coating stably when coating a coating solution having low surface tension and low viscosity, for example, a coating solution of an organic solvent type by the use of a bead-employing coating apparatus such as a coater of a slide hopper type or an extrusion coater. The inventors presumed that the cause of the difficulty lies in the under mentioned mechanism.

A coating apparatus such as a coater of a slide hopper type, a coater of an extrusion hopper type or a curtain coater is usually made of metal, especially of stainless steel. It has been made clear that wettability of a coating solution having low surface tension and low viscosity such as an organic solvent for metal is very high because the surface energy of metal is large and its critical surface tension is high. Therefore, a coating solution spreads over the surface of the metal and thereby a bead can neither be formed sufficiently nor be kept in a stable form, and thus, the coating solution spreads over the lip or its surroundings.

When a coating solution spreads more briskly, the coating solution oozes out even on an inclined surface following the lip portion where the coating solution gathers and drips on the coated layer or on the support, causing dropping defects problems.

Fig. 1 (a) is an illustrative sectional view showing an example of oozing out, and Fig. 1 (b) is a plan view. In the figure, the numeral 1 represents an extrusion coating die and 10 represents a slit through which a coating solution is supplied. The numeral 11 is a front bar and 12 is a back bar. Between web 2 running in the arrowed direction and the front and back bars, there is formed bead 13 through which a coated layer is formed on a web. In this case, oozing out of the coating solution impedes complete bead formation, and oozed out portion 14 is formed under the regular bead. When the oozed out portion grows larger, it touches the web, causing streak defects or comet defects, or causing edge dirt at uncoated portions on both sides of the support, or the oozed out portion becomes a dropping defects to cause a dropping defects.

The problems mentioned above are caused not only in a bead coater but also in a curtain coater. In a curtain coater, no bead is formed but a coating solution flows downward in the form of a curtain to hit a web, and the force of hitting the web causes a coated layer to be formed on the web. Even in this case of a curtain coater, there are two types, one is an extrusion type and the other is a slide hopper type. In the case of the former type, the coating solution oozes out on a lip as well as on an inclined surface following the lip at the slit outlet from which a flow-down layer comes out, and the oozed coating solution disturbs liquid releasing at the slit outlet, causing streak defects on the flow-down layer, or the oozed coating solution forms a drop which gets on the flow-down layer or drops on the web, resulting in dropping defects and streak defects.

Even in the case of a curtain coater of the slide hopper type, a coating solution oozes out on a beak-shaped lip portion and on its reverse side, and there are similar problems to those occurring on an extrusion coater.

To avoid such phenomenon of oozing out of a coating solution, it is necessary to use, as a lip portion and/or an inclined surface following the lip portion in a coating apparatus, a material having small surface energy and low critical surface tension whose water-repellent action prevents wetting, spreading and oozing out of a coating solution.

Though water-repellent resins such as Teflon or the like are used as an actual means for giving water-repellent property to a lip portion according to Japanese Patent Publication No. 57629/1989, it has been made clear that it is difficult to obtain the precision necessary for the lip of a hopper and to maintain the precision without damaging the lip even when a grinding step is taken for finishing the lip in the means for providing resins in the lip, although it is expected that Teflon is excellent in water-repellent property and it prevents a coating solution from oozing out and thereby prevents streak defects.

In the invention, it was found that composite plating wherein fine particles of fluorine-containing resin such as Teflon are dispersed in a form of eutectoid is very effective as a means which has water-repellent property and prevents streak defects and comet defects while correcting the aforementioned drawbacks. Due to the composite plating, it is possible to maintain the precision of a lip of a base material, which is a special feature of plating, and to form a coat having high hardness, while keeping the water-repellent property almost up to that of pure Teflon. A coating solution having low surface tension and low viscosity was coated at high speed by a hopper wherein a coat was formed on the surface of a lip portion and/or the surface of an inclined surface following the lip portion, and the occurrence of comet defects, streak defects and dropping defects were not observed at all.

Fluorine-containing resins to be made in a form of eutectoid are preferably those having excellent water-repellent property wherein a carbon chain in a polymer is covered by as many fluorine atoms as possible such as in polytetrafluoroethylene known as Teflon (made by Du Pont Corp. in the U.S.)

From the viewpoints of hardness, corrosion resistance and adhesiveness to a base material, it is preferable that nickel or chromium is used for a coat of plating wherein fluorine-containing resins is made in a form of eutectoid. It is further preferable that a lip portion for a coating die is plated by non-electrolytic plating utilizing a chemical reaction, from the viewpoints of uniformity of thickness of a plated coat, straightness and edge sharpness, which are required to be on a high level.

As a useful and concrete example of the so-called plating in the invention, there may be cited KANIFLON that is a trade name sold by Japan Kanigen Co., Ltd., as non-electrolytic nickel plating wherein Teflon fine particles, for example, are dispersed in a form of eutectoid. It is further possible to expect the effect of prevention of streak defects and others even for a coating solution having lower surface tension, due to more excellent water-repellent property obtained in the plating method developed by Applied Science Research Institute and C. Uyemura & Co., Ltd., wherein fluorine-containing resins are dispersed in a form of eutectoid.

After a coat of plating has been formed, it is preferable that the coat is subjected to heat treatment at a temperature of not less than 200 °C, and it is more preferable that the coat is subjected to heat treatment at a temperature ranging from 300 °C to 350 °C. The purpose of the above is to decompose, through heat treatment, the dispersing agents used for dispersing fluorine-containing resins uniformly in a plating solution so that the dispersing agents staying on the surface even after the formation of the coat of plating may not impede the water-repellent effect.

Portions to be plated include a lip portion of a hopper and an inclined surface following the lip portion, and it is preferable for coating that a length of the lower portion of a bead is substantially the same as that of a part of the lip positioned at an upstream side.

Namely, it is preferable that a material having critical surface tension which is lower than surface tension of a coating solution is used on the surface of a lip situated at the tip of a hopper.

The coating solution, in this case, concretely includes those for a photographic light-sensitive material layer, especially a photographic foundation layer, a light-sensitive material for a lithographic printing plate, a magnetic recording material and its foundation layer or a backcoating layer, and an electrophotographic light-sensitive material and so on.

Fig. 2 (a) to (f) are illustrative diagrams showing various coating apparatus and locations where problems tend to happen, that is, locations shown with thick lines to which the plating of the invention is to be applied.

Fig. 2 (a) is a sectional view of a coater of a slide hopper type, Fig. 2 (b) is a sectional view of a coater of an extrusion hopper type, Fig. 2 (c) is a sectional view of a curtain coater of a slide hopper type, and Fig. 2 (d) is a sectional view of a curtain coater of an extrusion hopper type, and the coat of plating of the invention is applied to each location. For the reason mentioned above, it is preferable to employ a coating method wherein a bead is adjusted so that a length of the bead may be equal to that of a part of the lip situated at an upstream side when only the inclined surface following the lip portion is subjected to plating on a coating apparatus of a hopper type. Fig. 2 (e) represents an explanatory diagram showing a preferable length of a lower portion of a bead in the case that only an inclined surface portion following a lip is plated, for extrusion type coating, while Fig. 2 (f) represents that for slide hopper type coating.

EXAMPLES

Effects of the invention will be illustrated as follows, referring to the examples.

Example 1

A coat of nickel plating of about 10 μm thick wherein Teflon fine particles are dispersed in a form of eutectoid was applied to a lip portion of a slide hopper coating apparatus, and a coating solution having the following composition was coated on a polyethylene terephthalate web having a thickness of 100 μm and a width of 300 mm.

After coating under the conditions of coating speed of 50 m/min, decompression degree of -20 mmaq and coating density of 20 ml/m^2, neither coating defects such as streak defects or the like nor abnormal coating thickness were observed, resulting in stable coating.

[Composition of coating solution]	parts by weight
Methyl ethyl ketone	50
Methanol	30
Ethyl acetate	10
Polymethylmethacrylate	1

Comparative example 1

After coating with a coater of the slide hopper type which is of the same type as in Example 1 but is not subjected to the aforementioned plating on its lip portion, there were caused streak defects and coating solution shortage that resulted in an uncoated portion in the form of a streak, independently of the level of the decompression degree, showing that the coating was unstable.

Example 2

A coat of nickel plating of about 10 μm thick wherein Teflon fine particles are dispersed in a form of eutectoid was applied to a lip portion of an extrusion hopper coating apparatus, and a coating solution having the following composition was coated on a cellulose acetate web having a thickness of 125 μm and a width of 300 mm.

After coating under the conditions of coating speed of 100 m/min, decompression degree of -30 mmaq and coating density of 23 ml/m^2, no coating defects such as streak defects or the like were observed, resulting in stable coating.

The straightness in the web width direction of the plated lip portion of the extrusion hopper coating apparatus mentioned above was 2 μm and variation of the coating thickness after coating was about 5%.

[Composition of coating solution]	parts by weight
Acetone	70
Isopropyl alcohol	20
Toluene	10
Cellulose acetate butylate	0.5

Comparative example 2

After coating with a coater of the extrusion hopper type which is of the same type as in Example 2 but is not subjected to the aforementioned plating on its lip portion, there were caused streak defects and coating solution shortage that resulted in an uncoated portion in the form of a streak, independently of the level of the decompression degree, showing that the coating was unstable.

Comparative example 3

After the lip portion of the coater of an extrusion hopper type which is of the same type as in Example 2 was lined with Teflon-containing resins and ground instead of being subjected to the aforementioned plating, coating was conducted. As a result, no coating defects such as streak defects were caused but the

straightness in the web width direction of the resin surface on the lip portion of the hopper was 12 μm and variation of coating thickness after coating was as high as about 30%.

Example 3

A coat of nickel plating of about 10 μm thick wherein Teflon fine particles are dispersed in a form of eutectoid was applied to an inclined surface portion following the lip portion of an extrusion coating apparatus wherein each of upper and lower lip lengths is 2.5 mm, and a coating solution having the following composition was coated on a cellulose acetate web having a thickness of 125 μm and a width of 300 mm.

[Composition of coating solution]	parts by weight
Acetone	70
Isopropyl alcohol	20
Toluene	10
Cellulose acetate butylate	0.5

(Coating conditions)

Coating speed: 60 m/min, decompression degree: -30 mmaq, coating density: 23 ml/m^2

As a result, a length of a lower portion of a bead was almost equal to that of the lip positioned at an upstream side, and neither coating defects such as streak defects nor coating thickness problem were caused, resulting in stable coating.

Due to the invention, it has become possible to provide a coating method which may offer uniform coating that is free from streak defects, dropping defects, and coating defects such as comet defects, even when a coating solution having low surface tension and low viscosity is coated with a coating die of a slide hopper type or with a coating die of an extrusion type.

Claims

1. A coating apparatus of a hopper type for coating one or more kinds of coating solutions on a running flexible support, said coating apparatus being provided with a slit wherein a lip portion at the tip of a hopper and/or an inclined surface following the lip portion are subjected to composite plating to be covered by a coat of the plating in which fluorine-containing resins are dispersed in a form of eutectoid.

2. The coating apparatus according to Claim 1 wherein a coat of plating wherein fluorine-containing resins are made in a form of eutectoid is based on non-electrolytic nickel plating utilizing chemical reaction.

3. The coating apparatus according to Claim 1 wherein said fluorine-containing resin is Teflon.

4. The coating apparatus according to Claim 1, wherein a coat of plating is subjected, after being formed, to heat treatment at a temperature of not less than 200 °C.

5. The coating apparatus according to Claim 1, wherein a coat of plating is subjected, after being formed, to heat treatment at a temperature of not less than 300 °C.

6. The coating apparatus according to Claim 1, wherein a coat of plating is subjected, after being formed, to heat treatment at a temperature ranging from 300 °C to 350 °C.

7. A coating method comprising a step for coating one or more kinds of coating solutions on a running flexible support wherein a coating apparatus in which an inclined surface portion following a lip portion at the tip of a hopper is provided with a coat of composite plating wherein fluorine-containing resins are dispersed in a form of eutectoid is used for coating under the condition that a length of a lower portion of a bead is almost the same as that of a lip positioned at an upstream side.

8. The coating method according to Claim 7 wherein a coat of plating wherein fluorine-containing resins are in a form of eutectoid is based on non-electrolytic nickel plating utilizing chemical reaction.

9. The coating method according to Claim 7 wherein said fluorine-containing resin is Teflon.

10. The coating method according to Claim 7, wherein a coat of plating is subjected, after being formed, to heat treatment at a temperature of not less than 200 °C.

FIG. 1 (a)

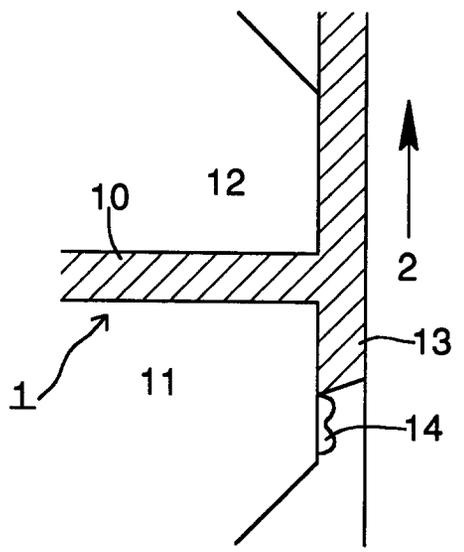


FIG. 1 (b)

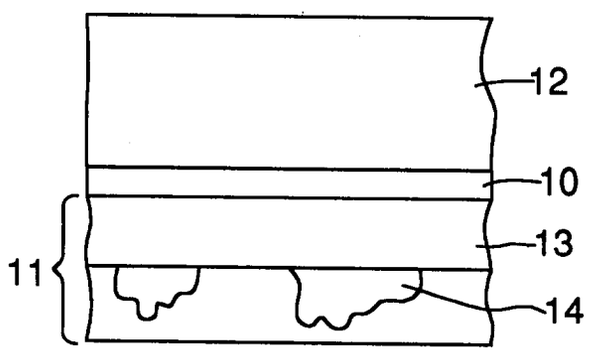


FIG. 2 (a)

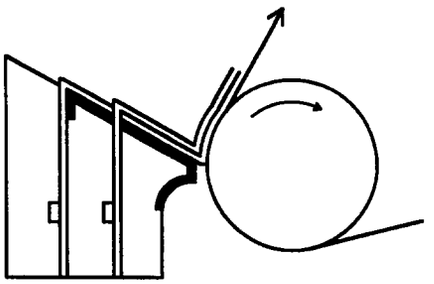


FIG. 2 (b)

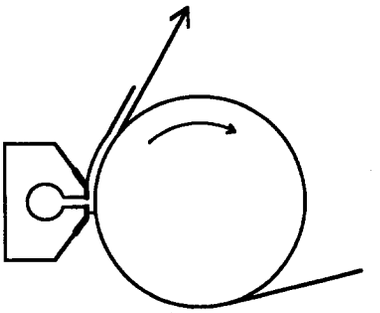


FIG. 2 (c)

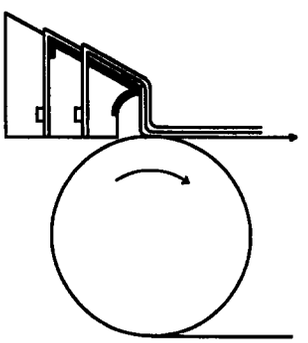


FIG. 2 (d)

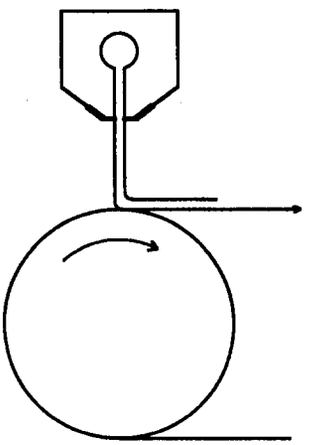


FIG. 2 (e)

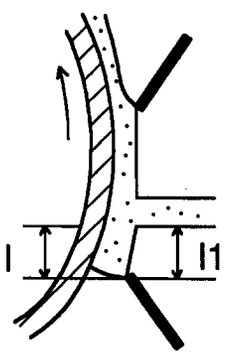
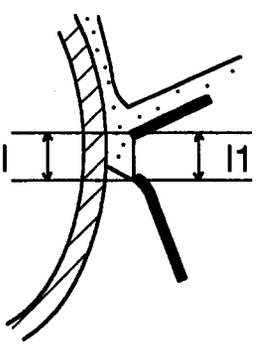


FIG. 2 (f)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00081

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 B05C5/02, B05C5/00, B05D1/26, B05D1/30

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)

Int. Cl^5 B05C5/00, B05C5/02, B05D1/26, B05D1/30, G03C1/74, G11B5/84, C23C18/52

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

Jitsuyo Shinan Koho 1926 - 1993
Kokai Jitsuyo Shinan Koho 1971 - 1993

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	JP, A, 59-189963 (Fuji Photo Film Co., Ltd.), October 27, 1984 (27. 10. 84), Claim (Family: none)	1-6, 7-10
Y	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No. 48251/1989 (Laid-Open No. 142667/1990), (Mitsubishi Heavy Industries, Ltd.), December 4, 1990 (04. 12. 90), p. 6, ℓ. 3 - ℓ. 10 (Family: none)	1-6, 7-10
Y	JP, A, 59-47399 (Uemura Kogyo K.K., Nippon Valqua Industries, Ltd.), March 17, 1984 (17. 03. 84), Claim (Family: none)	1-6, 7-10
Y	JP, A, 3-138376 (Koken K.K.), June 12, 1991 (12. 06. 91), Claim (Family: none)	1-6, 7-10

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"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
April 8, 1993 (08. 04. 93)	April 27, 1993 (27. 04. 93)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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