

686209

AUSTRALIA

SPRUSON & FERGUSON

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

Canon Kabushiki Kaisha, incorporated in Japan, of 30-2, 3-chome, Shimomaruko, Ohta-ku, Tokyo, JAPAN

[54] Invention Title:

Image Forming Method, Process for Producing Decorative Aluminum Plate, Apparatus for Carrying out the Process, Decorative Aluminum Plate, and Recording Medium

[72] Inventor(s):

Masami Ikeda, Tsutomu Abe, Keisuke Matsuo

[74] Address for service in Australia:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code SF)

	Details of Basic Application(s):	
[31] Appl'n No(s):	[33] Country:	[32] Application Date:
5-244762	JP	30 September 1993
6-162092	JP	14 July 1994
6-162093	JP	14 July 1994

Basic Applicant(s): Canon Kabushiki Kaisha

DATED this NINTH day of SEPTEMBER 1994

Canon Kabushiki Kaisha

By:



Registered Patent Attorney

S 049309 090994

IRIN 281439

INSTR CODE: 59510

PUBLISHED

SPRUSON & FERGUSON

Australia

Patents Act 1990

NOTICE OF ENTITLEMENT

Australian Patent
Application No. 72860/94

I, Giichi Marushima
care
of Canon Kabushiki Kaisha, 30-2, 3-chome, Shimomaruko, Ohta-ku, Tokyo, Japan

being authorised by the Applicant(s)/Nominated Person(s) in respect of an application entitled: Image Forming Method, Process for Producing Decorative Aluminum Plate, Apparatus for Carrying out the Process, Decorative Aluminum Plate, and Recording Medium
state the following:-

1. The Applicant(s)/Nominated Person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):- The Applicant/Nominated Person, by virtue of a Contract of Employment between the actual inventors as employees and the Applicant/Nominated Person as employer, is a person which would be entitled to have the patent assigned to it if a patent were granted on an application made by the actual inventors.

2a.* The Applicant(s)/Nominated Person(s) is/are the applicant(s) of the of the basic application(s) listed* on the Patent Request/ *in the Declaration under Article 8 of the PCT.

2b.* ~~The Applicant(s)/Nominated Person(s) is/are entitled to rely on the basic application(s) listed* on the Patent Request/ *in the Declaration under Article 8 of the PCT as follows:~~

3.* The basic application(s) listed *on the Patent Request/ *in the Declaration under Article 8 of the PCT is/are the application(s) first made in a Convention Country in respect of the invention.

4a.* ~~The Applicant(s)/Nominated Person(s) is/are the depositor(s) of the deposit(s) listed in the Schedule hereto.~~

4b.* ~~The Applicant(s)/Nominated Person(s) has/have the consent of~~, of

~~the depositor(s) of the deposit(s) listed in the Schedule hereto, to rely on that/those deposit(s).~~

DATED this

31st

day of August,

19 94

CANON KABUSHIKI KAISHA

(Signature) GIICHI MARUSHIMA:

Senior Managing Director

(Name & Title)

* Delete if not applicable.



AU9472860

(12) PATENT ABRIDGMENT (11) Document No. AU-B-72860/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 686209

- (54) Title
IMAGE FORMING METHOD, PROCESS FOR PRODUCING DECORATIVE ALUMINUM PLATE,
APPARATUS FOR CARRYING OUT THE PROCESS, DECORATIVE ALUMINUM PLATE, AND
RECORDING MEDIUM
- (51)⁵ International Patent Classification(s)
B41J 002/01 B41M 003/00 B41N 001/04 C09D 011/00
- (21) Application No. : 72860/94 (22) Application Date : 09.09.94
- (30) Priority Data
- | (31) Number | (32) Date | (33) Country |
|-------------|-----------|--------------|
| 5-244762 | 30.09.93 | JP JAPAN |
| 6-162092 | 14.07.94 | JP JAPAN |
| 6-162093 | 14.07.94 | JP JAPAN |
- (43) Publication Date : 13.04.95
- (44) Publication Date of Accepted Application : 05.02.98
- (71) Applicant(s)
CANON KABUSHIKI KAISHA
- (72) Inventor(s)
MASAMI IKEDA; TSUTOMU ABE; KEISUKE MATSUO
- (74) Attorney or Agent
SPRUIJON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001
- (56) Prior Art Documents
US 3558446
DE 3010532
GB 1449974
- (57) Claim

1. An image forming process for forming an image on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink containing a dye and a volatile component, comprising the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;

imparting ink to the anodic oxide layer having been subjected to heat treatment; and

removing the volatile component from the ink imparted and fix the dye into the anodic oxide layer.

1 Image Forming Method, Process for Producing
Decorative Aluminum Plate, Apparatus for Carrying
out the Process, Decorative Aluminum Plate, and
Recording Medium

5

BACKGROUND OF THE INVENTION

Field of the Invention

 This invention relates to an image forming
method by which characters, figured patterns, pictures
10 or the like are recorded on recording mediums having a
plate, sheet or foil made of aluminum or aluminum
alloy (hereinafter often simply "aluminum sheet"), as
exemplified by nameplates, display boards,
construction wall materials, automobile panels and
15 parts, tableware, aluminum cans and interior
decorative panels. It also relates to a process for
producing a decorative aluminum plate, an apparatus
used for carrying out such a process, and an
decorative aluminum sheet obtained by such a process.

20 The present invention sill also relates to an ink and
a recording medium that are used to make a record on
an aluminum anodic oxide layer.

Related Background Art

 As recording mediums for ink-jet recording,
25 paper is in general use. Those made of other than
paper are limited to plastic films provided on at

1 least one side thereof a layer endowed with ink
absorption properties by a special treatment. This is
considered due to the fact that ink-jet recording
apparatus have been mainly used for office work and
5 hence records are mostly made on paper serving as an
information medium and also that recording mediums are
required to have ink absorption properties and fixing
properties on account of the ink-jet recording system
in which ink droplets are caused to fly and adhere to
10 recording mediums.

Under such circumstances, as ink-jet recording
apparatus are made to have a higher speed and a higher
function, the application of ink-jet recording to
recording mediums made of materials other than paper
15 or plastic film is attracting notice. In particular,
ink-jet recording on metallic materials such as
aluminum or alloys thereof is expected not only to
make it possible to provide a simpler recording
process applicable on metallic materials, which can
20 substitute printing or the like, but also to promote
the expansion of use of articles made of metallic
materials and on which characters, patterns, pictures
or the like have been recorded.

Metallic materials utilized in a variety of
25 fields and uses may include aluminum and alloys
thereof. In particular, aluminum materials on the

1 surfaces of which anodic oxide layers, what is called
aluminum anodic oxide layers, are formed to improve
the corrosion resistance, surface strength and
decorativeness of aluminum have been hitherto used in
5 construction materials, tableware, panels for
electronic machinery, etc., and also in radiator
panels or the like utilizing good heat dissipation
properties of such layers. In particular, because the
aluminum anodic oxide layers can be colored with ease,
10 members having aluminum anodic oxide layers are also
used as decorated wallboard materials or door members,
as well as artistic decorations themselves. They are
also in wide use as personal nameplates of various
types.

15 As methods for coloring or recording on
aluminum anodic oxide layers (or anodic oxide layers),
photographic printing is in general use. In this
method, a series of steps of coating a resist,
exposing, developing, dipping in a recording solution
20 (dye solution) with a given color and stripping the
resist are repeated for each color to form a color
image by the use of multi-color recording solutions.

The photographic printing conventionally used
in the recording on the materials made of aluminum or
25 alloys thereof on which anodic oxide layers have been
formed requires a large number of processing steps,

1 which is complicated and takes a long time, and hence
the number of steps and the processing time greatly
increases with an increase in the number of colors of
the recording solutions. Thus, there is a limit to
5 the processing of a large quantity of materials.

Now, the ink-jet recording that enables color
recording at a high speed may be applied to such
processing. This makes it possible to greatly shorten
the processing time and more improve the productivity,
10 and also makes it unnecessary to use developing
solutions, washing solutions and so forth necessary
for the photographic printing, so that a great cost
reduction can be achieved. This also can solve the
problems of environmental pollution caused by, or
15 disposal of, waste liquors such as developing
solutions and washing solutions after their use.

The application of ink-jet recording to
aluminum anodic oxide layers is disclosed, for
example, in Japanese Patent Applications Laid-open No.
20 62-115074 and No. 3-147883. The methods disclosed in
these publications, however, are nothing but those in
which the conventional ink-jet recording is directly
applied to sheet materials having aluminum anodic
oxide layers.

25 In the ink-jet recording, ink wettability, ink
absorption properties and ink fixing properties of

1 recording mediums are especially important. If the
recording mediums have poor fixing properties, ink
droplets first shot for recording and ink droplets
subsequently shot for recording may mix to cause color
5 mixture to give no desired color reproduction and
sharpness. If the recording mediums have a poor
wettability on their surfaces, the ink may be repelled
on the surfaces, so that no good images can be
obtained.

10 However, the aluminum anodic oxide layers as
stated above are not necessarily satisfactory in
respect of the ink wettability, ink absorption
properties and ink fixing properties. Hence, the mere
direct application of ink-jet recording to aluminum
15 anodic oxide layers causes the following problems, and
can not necessarily be said to be practical.

The ink imparted to aluminum anodic oxide
layers is little absorbed in the anodic oxide layer,
and ink droplets mutually cause color mixture on its
20 surface, resulting in a blurred image. The aluminum
anodic oxide layers also have so poor ink fixing
properties that various rollers pertaining to the
transport of recording mediums and the control of
recording position in the ink-jet recording apparatus
25 may come in touch with the areas in which the ink has
not been fixed, and hence any marks of a roller rub

1 may appear on the surface to damage recorded images.

 Meanwhile, ink-jet recording carried out using
as an ink component a hitherto well known dye for
anodized aluminum also has the disadvantage that the
5 surfaces of aluminum anodic oxide layers can not be
well colored and no satisfactory colors can be
obtained especially in the case of deep colors.

 In addition, usual ink-jet recording, in which
a recording head having a number of nozzles carries
10 out simultaneous recording in order to increase
printing speed, has another disadvantage that, when
lines are recorded in an unfixed state, the ink of a
line first drawn is pulled toward the ink of a line
subsequently drawn, to cause a higher density at some
15 part for each line, that is, to cause uneven lines.

 Thus, it can not be said to be practical that
the high-speed color recording carried out by ink-jet
recording is directly applied to the recording mediums
made of materials other than paper or the like
20 conventionally used, e.g., those made of metals having
aluminum anodic oxide layers.

 Meanwhile, ink-jet recording apparatus used
for can manufacturing and for lot-number printing have
been put into practical use. Most of them, however,
25 make use of oil-based inks or pigment type inks, and
can not fly ink droplets having diameter small enough

1 to form highly minute images or tend to cause clogging
when nozzles are arranged in a high density. Thus,
the fields to which they can be applied are limited,
and they can not be said to be practical for the
5 recording of more highly minute images. Moreover, in
the ink-jet recording apparatus used for such
purposes, their nozzles can not have a sufficient work
precision and can only have a nozzle density of
several nozzles/mm at best. Hence, it has been
10 difficult to form more highly minute images and there
has been a problem in the image quality when applied
to decorative purpose. Thus, it also can not be said
to be practical that the ink-jet recording used in
this field is applied to the recording on aluminum
15 anodic oxide layers.

As discussed above, the mere application of
conventional ink-jet recording to the aluminum anodic
oxide layers of aluminum or alloys thereof has brought
about the following problems.

- 20 1) Mixing between colors (i.e, bleeding) may
occur to cause blurred images.
- 2) Uneven lines may occur in the recording scans
of recording heads.
- 3) Unfixed ink is transferred to transport
25 rollers and so forth inside the apparatus to cause
ghost images and crushed images.

4) Color ink has so poor a coloring ability to the aluminum anodic oxide layers that rinsing after printing may cause a decrease in image density, resulting in a low density.

Summary of the Invention

5 It is an object of the present invention to ameliorate one or more disadvantages of the prior art.

8
2
N

1
5
5
B



According to one aspect of the present invention there is provided an image forming process for forming an image on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink containing a dye and a volatile component, comprising the

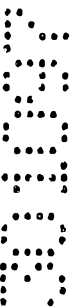
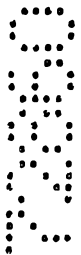
5 steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;

imparting ink to the anodic oxide layer having been subjected to heat treatment; and

removing the volatile component from the ink imparted and fix the dye into the

10 anodic oxide layer.



According to another aspect of the present invention there is provided a process for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink

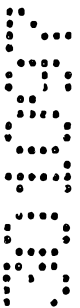
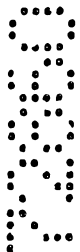
5 containing a dye and a volatile component, comprising the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;

imparting ink to the anodic oxide layer having been subjected to heat treatment; and

removing the volatile component from the ink imparted and fix the dye

10 contained in the ink into the anodic oxide layer.



According to still another aspect of the present invention there is provided an apparatus for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, comprising:

5 a first means for heating the aluminum plate, sheet or foil to dehydrate and activate the anodic oxide layer;

 a printing head provided adjacent to the first means, having a plurality of ink ejection orifices from which ink is applied to the anodic oxide layer in accordance with image printing signal, wherein ink comprises a dye and a volatile component;

10 a second means for heating the aluminum plate, sheet or foil to remove the volatile component from the ink applied and fix the dye contained in the ink in the anodic oxide layer; and

 a third means for transporting the aluminum plate, sheet or foil from the first means to the second means.

8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100



According to still another aspect of the present invention there is provided an image forming process for forming an image on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink containing a dye and a volatile component, comprising
5 the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;
imparting ink to the anodic oxide layer having been subjected to heat treatment by performing dot-interval printing by scanning a printing head plural times; and
removing a volatile component contained in the ink from the anodic oxide
10 layer to fix the dye contained in the ink into the anodic oxide layer.

8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100



According to yet another aspect of the present invention there is provided a process for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process, comprising the steps

5 of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;
imparting ink to the anodic oxide layer having been subjected to heat treatment
by performing dot-interval printing by scanning a printing head plural times; and
removing a volatile component contained in the ink from the anodic oxide
10 layer to fix a dye contained in the ink into the anodic oxide layer.

3
2
1
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100



- 1 at least one color from a recording head having a plurality of ink ejection orifices to an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, and a second
- 5 step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer on which the recorded image has been formed.

BRIEF DESCRIPTION OF THE DRAWINGS

- 10 Fig. 1 diagrammatically illustrates the structure of an anodic oxide layer of aluminum or an alloy thereof.

- Figs. 2A to 2C and 2D to 2F each illustrate the surface configuration of an aluminum or aluminum
- 15 alloy material and how bleeding occurs or does not occur.

Fig. 3 illustrates a manner of the storage of a recording medium on which the anodic oxide layer has been formed.

- 20 Fig. 4 also illustrates a manner of the storage of a recording medium on which the anodic oxide layer has been formed.

- Fig. 5 still also illustrates a manner of the storage of a recording medium on which the anodic
- 25 oxide layer has been formed.

Fig. 6 is a graph to show the state of



1 evaporation of a solvent commonly used in ink-jet
recording inks.

Fig. 7 diagrammatically illustrates the main
part of an example of the ink-jet recording apparatus
5 of the present invention.

Fig. 8 illustrates an example of the
construction of a tray used in the ink-jet recording
apparatus of the present invention.

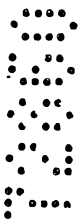
Fig. 9 illustrates an example of a position
10 correcting system operable in accordance with the
temperature of the image forming surface of a
recording medium when the recording medium and a
recording head are positionally registered in the ink-
jet recording apparatus of the present invention.

15 Fig. 10 illustrates a specific example of the
formation of dots on a recording medium in the ink-jet
recording of the present invention.

Figs. 11A to 11D illustrate specific examples
in which patterns are changed in 1st-pass to 4th-pass,
20 respectively, for a black color to make a record in
the ink-jet color recording of the present invention.

Figs. 11E to 11H illustrate specific examples
in which patterns are changed in 1st-pass to 4th-pass,
respectively, for a cyan color to make a record in the
25 ink-jet color recording of the present invention.

Figs. 12A to 12D also illustrate specific



1 examples in which patterns are changed in 1st-pass to
4th-pass, respectively, for a magenta color to make a
record in the ink-jet color recording of the present
invention.

5 Figs. 12E to 12H illustrate specific
examples in which patterns are changed in 1st-
pass to 4th-pass, respectively, for an yellow color to
make a record in the ink-jet color recording of the
present invention.

10 Fig. 13 perspectively illustrates an example
of an apparatus for carrying out the ink-jet color
recording of the present invention.

Figs. 14A and 14B illustrate an ideal state of
image formation on a recording medium.

15 Figs. 15A and 15B illustrate an improper state
of image formation on a recording medium.

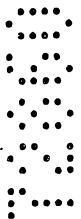
Figs. 16A to 16G illustrate how dots come
together after their impact onto a recording medium.

20 Figs. 17A and 17D illustrate how dots run over
after their impact onto a recording medium.

Figs. 18A to 18L illustrate a manner by which
an image is formed on a recording medium according to
the present invention.

25 Figs. 19A to 19F also illustrate a manner by
which an image is formed on a recording medium
according to the present invention.

Fig. 20 illustrates a dot-interval drive



1 according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The recording medium according to ^{an embodiment} ~~the present~~
5 ~~invention~~ comprises an anodic oxide layer formed on
the surface of a plate, sheet or foil made of aluminum
or an alloy thereof. The recording medium may also
have a laminated structure in which the plate, sheet
or foil made of aluminum or an alloy thereof is
10 provided on a base comprised of a material other than
aluminum or an alloy thereof, including various
materials (substrate materials) as exemplified by a
clad material.

15 Regarding the aluminum or an alloy thereof
^{this embodiment,} ~~used in the present invention,~~ there are no particular
limitations thereon so long as they are well capable
of forming the anodic oxide layer. For example, it is
possible to use sheet or foil materials of a pure
aluminum type such as those prescribed in JIS-1050 and
20 sheet or foil materials made of an aluminum alloy used
for anodized aluminum, such as an alloy containing Mg.

The surface of the plate, sheet or foil made
of aluminum or an alloy thereof which is a material
worked in desired shape and size by means of a press
25 machine or the like so as not to cause any
unauthorized deformation such as warpage or flashes



1 and on which the anodic oxide layer is formed to
provide an image forming surface, may preferably be
treated, if necessary, by a mechanical means or
chemical polishing to control its surface properties
5 so that good images can be formed in the course of
recording. This surface treatment can be exemplified
by a treatment of providing concavities smaller than
ink droplets and having ridges along their
peripheries, over the whole image forming surface.
10 Such a surface treatment makes it possible to prevent
ink, having impacted on a desired position, from
mixing with ink having impacted on other regions or
moving to other regions to cause bleeding. In
particular, since aluminum sheet materials commonly
15 available are rolled materials, marks (grooves) of
rolling extend in one direction, and the ink tends to
run along the marks of rolling, so that inks tend to
cause color mixture in the direction of rolling.
Accordingly, the concavities with a diameter smaller
20 than the ink droplets are formed over the whole
surface, whereby such color mixture can be prevented.
The diameter of a concavity may be set in accordance
with the diameter of an ink droplet. For example, ink
droplets each have a diameter of about 100 μm under
25 recording conditions of 360 dpi, and hence any surface
treatment method that can make a concavity having a

1 diameter of smaller than 100 μm may be selected and
used. Figs. 2A through 2C, along stages Figs. 2A to
Fig. 2C thereof, diagrammatically illustrate a
mechanism by which the bleeding can be prevented on
5 the surface provided with such concavities. Figs. 2D
through 2F, along stages Fig. 2D to Fig. 2F thereof,
diagrammatically illustrate typical examples in which
the bleeding occurs. In Figs. 2A and 2D, reference
numeral 21 denotes ink droplets; 22, an anodic oxide
10 layer; and 23, an aluminum plate.

This surface treatment can be made using a
mechanical working process in which a beads type
abrasive is sprayed on the surface, e.g., shot
blasting, or a chemical process making use of an
15 etching solution. The treatment may preferably be
made by chemical polishing that can effectively form
concavities having ridges around their peripheries on
account of the generation of gas and the presence of
grain boundaries at the time when the recording medium
20 is immersed in an etching solution.

The surface of the material on which the
anodic oxide layer is to be formed is further
optionally subjected to degreasing and pickling that
are commonly carried out, and thereafter the anodic
25 oxide layer is formed by anodizing in, for example, a
sulfuric acid bath, followed by rinsing with water.

- 1 The anodic oxide layer is formed in a layer thickness
of, for example, from 5 to 25 μm .

Fig. 1 diagrammatically illustrates the
structure of an anodic oxide layer of aluminum or an
5 alloy thereof. An anodic oxide layer 1 formed on the
surface of a base 4 comprised of aluminum or an alloy
thereof is constituted of a large number of cells 3,
and a pore (a minute opening) 2 is formed
substantially at the center of each cell. The bottom
10 of this pore 2 is constituted of a barrier layer 5
located at the boundary between the pore and the base
4.

Accordingly, the larger diameter the pore has,
the higher the coloring ability and ink receptivity
15 become. Also, the deeper the pore is, the higher the
ink receptivity becomes. Hence, as conditions for
electrolysis in the anodizing, it is preferable to
select conditions under which pores can be formed in
such a state.

20 The diameter or depth of the pore 2 can be
increased by a treatment made at a higher temperature
or using an electrolytic solution with a higher
density. If, however, the thickness of the barrier
layer 5 becomes smaller, the material may cause a
25 decrease in its own corrosion resistance. Hence, the
conditions for electrolysis should be selected taking

1 account of these factors.

For example, as the composition of the electrolytic solution, a solution of 10 to 30% (weight ratio) of sulfuric acid is prepared. A SUS (a kind of stainless steels) plate is used as the cathode, and an aluminum sheet having been subjected to the pretreatment described above and also subjected to degreasing, rinsing with water and desmutting before the anodizing is set on the anode. In an electrolytic bath controlled to have a bath temperature of about 25°C and also well agitated, the anodizing is carried out at a current density of from 60 to 300 mA/m² for a suitable time until the required layer thickness is achieved. Thereafter, the treated product is taken out of the electrolytic bath, thoroughly rinsed with water, dried, and then stored.

The above electrolysis may be divided into two stages, where conditions under which large-sized pores are formed are employed in the first stage and conditions under which small-sized pores are formed are employed in the second stage so that the barrier layer can be made to grow on the substrate side to improve corrosion resistance. Such a method is also effective. In this case, the treatment at the second stage may be carried out in the same bath as that for the first stage, or may be carried out in a bath

1 different from that for the first stage. In order to
grow the barrier layer, it is also effective to use a
boric acid type electrolytic solution.

In this way, the image forming surface
5 comprised of the anodic oxide layer is formed on the
surface of the base comprising the plate, sheet or
foil of aluminum or an alloy thereof. The recording
medium thus obtained is stored if necessary, and
thereafter treated in the first step of ink-jet
10 recording carried out in the image forming method of
the present invention.

When the recording medium is stored, the state
of its storage may greatly influence the operation of
image formation and the state of storage should
15 preferably be controlled so as to be suited for the
desired end. As described in relation to Fig. 1, the
anodic oxide layer is constituted of a number of cells
having pores, and the presence of these pores makes it
possible for the ink to be absorbed into the layer to
make a record. If, however, the anodic oxide layer is
20 left to stand in an atmosphere containing water
(vapor) and oxygen as in the air, a hydroxide is
formed on the layer as a result of the reaction of
water with oxygen. If it is formed in the pores, the
25 pores becomes narrow or may be closed. As the
reaction proceeds, almost all the pores in the layer

1 are brought into the state of being closed. A
decrease in pore volume or the closure of pores
results in a decrease in ink receptivity (ink
absorption), and brings about the problem that the
5 image quality tends to deteriorate because of
occurrence of bleeding and color mixture. Hence, in
the storage of the recording medium, it is preferable
to shut off water content and oxygen. As a manner of
storing the recording medium, the recording medium may
10 preferably be stored in a container into which
nitrogen gas can be flowed to form an atmosphere of
nitrogen gas, be stored in a container into which a
moistureproofing agent such as silica gel or a
deoxidizing agent can be put to form an atmosphere of
15 dry air, or be kept away or shut off from the open
air.

Examples of the manner of storage are shown in
Figs. 3 to 5. Fig. 3 shows a storage box 32 provided
with a nitrogen gas blow pipe (an N_2 blow pipe) 33,
20 where the inside of the box is replaced by nitrogen so
that the recording medium 31 can be stored. Fig. 4
shows a bag 34 made of resin, in which a deoxidizing
agent 35 is put together with the recording medium 31
for its storage under a sealed state. The manner of
storage shown in Fig. 5 is a manner in which the
25 surface of an anodic oxide layer 31-1 formed on a base

1 31-2 comprised of aluminum or an alloy thereof is
covered with an adhesive tape 35 comprised of an
oxygen and vapor barrier film 36-1 such as
polyethylene terephthalate film and an adhesive layer
5 36-2 formed on its surface to hermetically seal the
former so that the recording medium can be stored in
the state it is kept away from its contact with the
atmosphere.

In the first step of the ink-jet recording of
10 the present invention, the anodic oxide layer
constituting the surface of the image forming surface
of the recording medium is dehydrated and activated.

This treatment causes the aluminum anodic
oxide layer to undergo dehydration and condensation of
15 the water content adsorbed on boehmite $\text{AlO}(\text{OH})$ and
alumina $\gamma\text{-Al}_2\text{O}_3$ formed on the outer surface when the
layer is formed, so that activation points are formed
thereon. The activation points react with water
content in the atmosphere and behave so as to
20 immediately return to the original state. Hence, it
is important for this treatment to be carried out
immediately before the step of recording. Once the
activation points have been formed, reactive groups of
the dye contained in the ink combine at these points,
25 so that the coloring ability is improved. There is
also an advantageous effect that the water content in

1 the ink is absorbed to increase the quantity of ink
reception.

In this first step, a heat treatment, an
electromagnetic induction treatment or a treatment by
5 dry-air blowing can be utilized. In the dry air,
active gas such as H_2 or O_3 may be mixed. A method of
applying a charge treatment by corona discharging may
also be used.

10 Stated specifically, for example, dry air
heated to $60^\circ C$ is blown on the aluminum anodic oxide
layer at a rate of about 20 liter/min through an
opening of 20 cm $\times$ 5 cm. The aluminum sheet on which
this aluminum anodic oxide layer has been formed is
passed through the above opening at a speed of about
15 30 cm/min, and then transported to an ink-jet
recording zone. Since this treatment can not be well
effective if the atmosphere or the aluminum sheet has
a low temperature, a tray for the transport may
preferably be provided with a sheet heater so that the
20 sheet can be preliminarily heated up to about $60^\circ C$.

At the time the treatment in the first step
has been completed, ink-jet recording (the second
step) is carried out on the recording medium. In the
ink-jet recording in the second step, any recording
25 apparatus and recording system applied to usual
recording mediums such as paper can be used.

1 With regard to ink, there are no particular
limitations thereon so long as it can achieve the
desired end. An ink making use of a coloring matter
(a dye) having a good coloring ability to the anodic
5 oxide layer is preferred. More specifically, in the
case of the anodic oxide layer of aluminum or an alloy
thereof, the oxide layer is formed by anodizing
carried out under application of a direct current or
an alternating current in an electrolytic solution of
10 sulfuric acid or the like, setting the aluminum or an
alloy thereof to serve as the anode. Hence, the layer
is in a state of still containing many kinds of
intermediate products formed when the aluminum or an
alloy thereof is changed into its oxide in the course
15 of the dehydration and condensation in the anodizing
reaction. The intermediate products are rich in
reactivity (e.g., boehmite). Thus, use of a dye
highly reactive with such intermediate products
enables improvement of the coloring ability. Such a
20 dye may include, for example, dyes having at least one
kind of anionic groups. In particular, dyes having a
carboxyl group and/or a sulfonic group are preferred.

 The pH of the ink may preferably be on the
alkaline side rather than the acid side. This is
25 presumably because the layer is formed on the anode
side and tends to be dissolved on the alkaline side.

1 With regard to solvent components of the ink,
there are no particular limitations thereon so long as
it can achieve the desired end. However, nonvolatile
solvents such as glycerol utilized in conventional ink-
5 jet recording inks used on paper or the like and
glycols having a high molecular weight remain on the
image forming surface after volatile solvents have
been evaporated, as shown, for example, in Fig. 6.

Fig. 6 graphically show an evaporation loss
10 with time, of an ink containing a non-volatile
solvent. Fig. 6 shows the evaporation loss of the ink
put in a laboratory dish under dry conditions of 60°C.
The evaporation loss is indicated on the ordinate, and
the time, on the abscissa. First, volatile components
15 evaporate when the ink is put in at 60°C, and the
evaporation loss increases with the rate of
evaporation, where the quantity of ink is kept
constant when the volatile components have completely
evaporated and only non-volatile components have
20 remained. If it is a quantity more than that
acceptable in cells, the surrounding ink droplets may
mutually mix to cause bleeding, possibly resulting in
a deterioration of image quality.

In the case of paper, cloth or recording
25 mediums so constructed that a base material of the
image forming surface is capable of absorbing

1 solvents, such non-volatile solvents permeate into the
base material and hence have no influence, or only an
influence small enough to be ignorable, on the dyes
constituting the image on the surface layer. On the
5 other hand, the permeation of non-volatile solvents in
the direction of the base material as in the case when
paper or the like is used do not occur in the case of
the anodic oxide layer formed on the surface of
aluminum or an alloy thereof, and hence the solvents
10 remain in the layer to often cause color mixture,
blur, bleeding or the like. Inks prepared using only
water and dyes can not be endowed with a viscosity
suitable for the generation of bubbles in apparatus
and for the recording. For such reasons, the use of
15 such non-volatile solvents in ink is indispensable for
enabling effective operation of ink-jet recording
apparatus. Accordingly, in order to prevent the
problems caused by non-volatile solvents, the content
of a non-volatile solvent in ink may preferably be so
20 controlled that the non-volatile solvent holds a
volume smaller than the total volume of the pores
present in the region where ink droplets impact
against and spread on the image forming surface.

The ink absorption in the anodic oxide layer
25 is governed by the volume of pores. Hence, in the ink-
jet recording of the present invention the dye in ink

1 may preferably be in a shot-in quantity set in
accordance with the structure of the anodic oxide
layer constituting the image forming surface, in
particular, in accordance with the volume of pores.
5 For example, when the anodic oxide layer having the
structure as shown in Fig. 1 has a cell diameter of
about 400 angstroms, a pore diameter of about 100
angstroms and a pore depth of about 10 μm and the
recording is carried out under conditions of 400 dpi,
10 it follows that one picture element has a side of
about 63 μm and hence about 2,400,000 cells are
present in it, having pores with an internal volume of
about 0.0008 μm^3 per pore. Thus, the total volume of
the pores per picture element comes to be about 1,900
15 μm^3 . A value obtained by dividing this total volume
by the area of one picture element is a reception
height, which comes to be 0.46 μm . In this case, the
dye concentration in ink is governed by this reception
height. In the case when the volume per unit ink
20 droplet (ejection quantity) is 30 ng, the reception
height of 0.43 μm gives a dye concentration of about
3%. From the viewpoint of the degree of coloring and
the reflection O.D. (optical density) at colored
areas, the reception height may preferably be 0.2 μm
25 or more in order to obtain sharp images. In the
formation of the anodic oxide layer, the conditions

1 for analysis should be so set that the layer
thickness, cell density and pore size that satisfy
this reception height can be obtained.

In setting conditions as described above, when
5 the ink ejection quantity is 30 ng and the reception
height (hereinafter also often "reception quantity")
of the aluminum anodic oxide layer is 0.46 μm , what is
important is that the tolerance of non-volatile
components contained in the ink is not more than the
10 above reception quantity of the layer. Thus, it has
become clear that the image bleeding can be prevented
when the non-volatile solvent is controlled to be
mixed in an amount of 6% by weight or less.

This amount depends on the shapes of cells and
15 pores and the layer thickness of the anodic oxide
(anodized aluminum) layer. Namely, when the layer
thickness is about 20 μm , the non-volatile solvent can
be mixed in an amount at least twice as much as the
foregoing. When the cells are in a high density and
20 also when the pores are large in size, it can be mixed
in a much greater amount. However, its upper limit is
about 10% in the case of usual aluminum anodic oxide
layers, and should preferably be in an amount of 5% or
less.

25 If the non-volatile solvent is completely
removed, the ink-jet recording head may clog or the

1 first-ejection performance may become poor, rather
often resulting in a deterioration of image quality.
Hence, it is important for the non-volatile solvent to
be mixed in an optimum amount within the above range.

5 The non-volatile components mentioned above
are comprised of dyes, as well as diethylene glycol,
triethanolamine, polyethylene glycol, glycerol, urea
or the like. They may be any kinds of solvents and
additives so long as they have a good I/J (ink jet)
10 suitability and do not adversely affect the printing
on aluminum anodic oxide layers.

In the bubble-jet recording, the volatile
components mentioned above are solvents capable of
bubbling upon heating, which may include water, IPA,
15 acetone and alcohols, and may be any solvents so long
as they have a good I/J suitability and do not
adversely affect the printing on aluminum anodic oxide
layers.

The volatile components should preferably have
20 an evaporation rate ranging from 1.0×10^{-5} g/mm².sec
to 1.0×10^{-7} g/mm².sec in the state that all solvents
have mixed and in a dry environment of 60°C. Here,
ink droplets shot in the aluminum anodic oxide layer
surface completely evaporate in a time of from several
25 seconds to several ten seconds, so that the ink
droplets become dry in one scan to several scans and

1 high-quality images can be recorded without blur or
bleeding.

At the time the ink-jet recording has been
completed, the image formed on the image forming
5 surface is subjected to the third step, i.e., the step
of evaporating the solvent components in the anodic
oxide layer, on which the image has been formed, so
that dye components of the ink can be fixed.

In this third step, the coloring component
10 contained in ink is the dye. Other components are
components necessary at the time of ink-jet recording
and are components unnecessary after the aluminum
anodic oxide layer has been colored. Hence, such
unnecessary components must be removed as soon as the
15 dye in ink has been received in the cells after
recording and its dyeing reaction with the layer has
been completed.

First, in order to make the dye and the layer
undergo fixing reaction in a good efficiency, it is
20 important to heat the layer itself to accelerate the
reaction. Next, in order to deposit the dye in the
pores of cells, the volatile components in the ink
should be made to evaporate as soon as possible to
retain the dye in the cells. This is important for
25 the formation of images with a high quality.

The ejection quantity is usually so designed

1 as to provide a maximum recording density, and hence
the dye is contained in an amount set at a maximum
value of the reception quantity of the coating.
Since, however, the head may eject the ink in a
5 greatly uneven quantity, a phenomenon may occur such
that the ink is shot in a quantity more than the
reception quantity of the coating. Moreover, to form
an image, multi-color inks can be shot in the same
site, and a dye itself may become an unnecessary
10 component, which therefore remains on the layer. When
the dye remains on the layer in this way, the dye may
exude when sealing is subsequently applied in order to
improve corrosion resistance of the aluminum anodic
oxide layer. This may cause a deterioration of image
15 quality, or, if the product is used as it is, the dye
may similarly exude in an environment in which
resistance to water or sweating is required, resulting
in no durability for image quality.

20 An example of a specific manner by which the
components unnecessary after recording as stated above
will be described below.

25 First, the aluminum sheet on which the
aluminum anodic oxide layer has been formed and having
been subjected to the ink-jet recording is heated with
three infrared lamps of 500 W from the upper part
while it is passed over a heat sheet of 1,000 W at the

1 lower part, which is passed at a rate of travel of
about 30 cm/min. In this example, four colors of Y,
M, C and Bk are superimposingly shot. Accordingly,
the recorded surface is rinsed with pure water as a
5 post-treatment to remove excess dyes, followed by
drying to obtain an image-recorded product.
Thereafter, this image-recorded product is immersed
for 10 minutes in boiling pure water of about 100°C,
to carry out sealing of the aluminum anodic oxide
10 layer, followed by drying to obtain a finished
product.

In the present invention, at the time the ink-
jet recording has been completed, an aqueous
polyvalent metal salt solution may be applied to the
15 image formed on the image forming surface. This makes
it possible to produce an image-recorded product
having a fastness to light.

The aqueous polyvalent metal salt solution
comprises polyvalent metal cations such as Cu^{++} , Ni^{++}
20 and Al^{+++} . Examples are by no means limited to these,
and other polyvalent metal cations may be used so long
as the same effect can be obtained.

As anions that combine with such cations
include Cl^- , ClCO_3^- and CH_3COO^- . Of course, examples
25 are by no means limited to these.

This aqueous polyvalent metal salt solution

1 should have a salt concentration of from 0.05 to 50%
by weight, and preferably from 0.2 to 30% by weight.

 The polyvalent metal cations in the solution
react with the reactive groups of the dye, e.g.,
5 carboxyl groups and sulfonic groups, to form a dye
complex. As previously stated, dyes highly reactive
with intermediate products, in particular, dyes having
reactive groups such as carboxyl groups or sulfonic
groups are preferred. Use of such dyes facilitates
10 the reaction with polyvalent metal cations, so that
the dye complex can be formed with ease. The
formation of such a dye complex can prevent
decomposition of dye molecules and prevent any
discoloration or color change due to changes with
15 time.

 As a method for applying the aqueous
polyvalent metal salt solution to the image formed on
the image forming surface, the aqueous polyvalent
metal salt solution may be sprayed on the anodic oxide
20 layer by means of a sprayer or the like, in case of
the use as an interior decoration. It is more
preferable to wash the anodic oxide layer with the
aqueous polyvalent metal salt solution.

 When image-recorded products are used outdoors
25 and require a reliability, it is preferable to carry
out sealing of the anodic oxide layer using the

1 aqueous polyvalent metal salt solution.

The relationship between the aluminum anodic oxide cell configuration and the shot-in ink quantity will be further detailed below.

5 In the aluminum anodic oxide cell structure as shown in Fig. 1, diameter of the cell is $A \mu\text{m}$, diameter of the pore formed in the cells is $a \mu\text{m}$, and layer thickness is $L \mu\text{m}$. Here, the respective aluminum anodic oxide cells are arranged in the form
10 of substantially regular hexagons and hence have a cell surface area S_c of:

$$S_c = \frac{3\sqrt{3}}{8} A^2 (\mu\text{m}^2)$$

15 and a pore surface area S_p of:

$$S_p = \frac{\pi}{4} a^2 (\mu\text{m}^2)$$

20 Therefore, an area proportion C_p held by pores is:

$$C_p = \frac{2\pi}{3\sqrt{3}} \left(\frac{a}{A} \right)^2$$

25 Therefore, when the barrier layer 5 is disregarded, an ink reception height $R_a (\mu\text{m})$ per unit area is:

1

$$R_d = L * C_P = \frac{2\pi}{3\sqrt{3}} \left(\frac{a}{A} \right)^2 L \text{ (}\mu\text{m)}$$

Here, when the volume of ink droplets to be shot in is represented by V_d (μm^3) and the shot-in area by S_d (μm^2), the height h (μm) per unit area, of the ink droplets having been shot in, is:

$$h = V_d / S_d.$$

Here, also when the volume percentage held by non-volatile components in the ink (mixing ratio) is represented by X , a non-volatile component height t (μm) is:

$$t = X V_d / S_d \text{ (}\mu\text{m)}.$$

It is important for the height t not to exceed the ink reception height R_d set forth above. If $t \leq R_d$ is not satisfied, the ink may exude to cause a deterioration of image quality as previously stated. Therefore, it is important to select the mixing ratio X and the layer thickness L so that;

20

$$X V_d / S_d \leq \frac{2\pi}{3\sqrt{3}} \left(\frac{a}{A} \right)^2 L$$

that is;

25

$$X V_d / S_d \leq 1.21 \left(\frac{a}{A} \right)^2 L$$

1 is satisfied. Also, since in general the V_d/S_d is 10
μm and the a/A of the aluminum anodic oxide layer is
0.25 in ink-jet recording, it usually follows that;

$$X \leq 0.0076L^*$$

5 wherein L^* is a dimensionless number.

An example of the production apparatus
employing the above ink-jet recording of the present
invention will be described below.

Fig. 7 diagrammatically illustrates the whole
10 production apparatus. In Fig. 7, reference numeral
710 denotes a recording head, which is an ink-jet
recording head with 128 nozzles of 400 dpi, having an
ejection quantity of 25 ng per dot. The apparatus is
provided with four recording heads corresponding to
15 four colors of Y (yellow), M (magenta), C (cyan) and
Bk (black) and is so set up that a full color image
can be recorded at one scan. Reference numeral 701
denotes a recording medium comprising, as previously
described, a plate, sheet or foil made of aluminum or
20 an alloy thereof on the surface of which the anodic
oxide layer has been formed to serve as the image
forming surface. A plurality of recording mediums 701
are set in a stocker 711, which are successively sent
to a belt conveyor by means of a transporter 712 and
25 fed forward to a printing tray 715. Reference numeral
714 denotes an auxiliary roller for transport.

1 The recording medium 701 fed to the printing
tray 715 is firmly secured by suction onto the tray by
the operation of a suction pump 716. The recording
medium 701 on the tray 715 is sent to a zone where the
5 first treatment step (the step of dehydration and
activation) is carried out, and is heated by
irradiation with infrared rays from infrared lamps
704, so that the water content present in the anodic
oxide layer of the recording medium 701 is removed and
10 also dehydration reaction take place to activate the
layer. A fan 705 is also rotated to ventilate the
zone, whereby the treatment at the first step can be
made more effective.

 The recording medium 701 is sent out by the
15 operation of a feed motor 717 from the zone of the
first treatment step, and immediately thereafter the
recording head 710 carries out ink-jet recording. In
this second step ink-jet recording, various ink-jet
recording systems such as a piezoelectric type and an
20 electrostatic type can be used. A bubble-jet
recording system is preferred since it can stably
carry out high-speed recording.

 As for the recording process, two-pass or four-
pass printing may be employed if the problem of
25 bleeding or the like occurs when one-pass printing is
employed. As inks used here, those having various

1 composition can be used. As previously stated, those
in which the types of dyes and the content of non-
volatile solvents have been suited for use in anodic
oxide layers may preferably be used under appropriate
5 selection. The recording medium 701 on which an image
has been recorded is immediately transported to a zone
in which the third step treatment is applied. This
step is taken in order to evaporate and send off the
volatile components of inks present in the anodic
10 oxide layer on which an image has been formed, and
also allow the dyes in inks to react with the layer to
promote dyeing so that the image can be firmly fixed.
In this apparatus, this third step is carried out by a
heating means 703 having a fan and infrared lamps in
15 combination. What is intended in the third step is to
fix the dye in the inks on the layer. It is also a
process preferable for fixing dyes that the water and
oxygen in the air react with the anodic oxide layer to
form a hydroxide to seal pores in the layer. Hence,
20 different from the first step, it is not always
necessary to operate the fan.

The recording medium 701 (an image-recorded
product) having been subjected to the above three
steps is transported to a stocker 719 via a conveyor
25 720 and a feed roller 721, and received at a given
position by a handler 718.

1 In the example shown in the drawing, the
recording medium 701 has the shape of a rectangular
sheet. The tray 715 on which it is transported is
appropriately adjusted so as to be conformable to the
5 form of the recording medium. For example, a spacer
811 as shown in Fig. 8 may be used so that the tray
can be adapted to the recording on a disk type
recording medium. This apparatus may also preferably
have a means for adjusting the distance between the
10 recording head and the image forming surface of the
recording medium in accordance with the thickness of
the recording medium.

 In order to promote the effect of the heating
in the first step and the third step, the tray may be
15 auxiliarily provided with a heating means such as a
heater so that, for example, the recording medium is
preheated before each treatment. This improves
heating efficiency also when a relatively large-sized
recording medium with a large heat capacity is
20 treated, and enables effective treatment.

 When the recording medium is heated, any
dimensional distortion may occur because of thermal
expansion to cause a deviation in the width direction
of recording and the feed direction, bringing about
25 the problems of white stripes appearing on recorded
images and deviation of print size. In such a case,

1 it is preferable to use, for example, as shown in Fig.
9, a system in which the surface temperature of the
image forming surface of a recording medium 901 is
detected by a temperature sensor 902, the detected
5 values are amplified by an amplifier (Amp), the
amplified values are digitized using an A/D converter
(A/D) to compare the digitized value with a preset
value by means of a comparator and then the signals
obtained are sent to a recording head 910 and a motor
10 903 in the form of optimum delay signals with respect
to clock signals to make control so that the recording
medium can be correctly positioned.

As previously stated, in the anodic oxide
layer of aluminum or an alloy thereof, the ink
15 reception quantity is greatly influenced by the
sealing percentage of the pores constituting the
layer, the layer thickness, the pore size, the cell
density and so forth. However, these properties of
the layer may become non-uniform among a plurality of
20 recording mediums formed under the same conditions,
and may cause a non-uniformity in image quality, in
particular, a non-uniformity in image quality between
lots when the recording is carried out in the second
step under the same conditions. In such a case, the
25 problem can be solved by adding a control means for
adjusting the ejection quantity by controlling

1 recording head pulse width, head temperature, time
between full pulses and so forth, on the basis of a
feedback of the results obtained by previously
printing characters on the anodic oxide layer at its
5 part on which no images will be recorded and pre-
examining their print density, balance of shade
between colors and so forth.

In order for the recording medium to be
transported in a good precision, a mark may be made at
10 a non-print area of the recording medium by etching or
pressing so that its position can be read by a
suitable reading means to always make sure the
position of the recording medium and control the
transport means in accordance with the position,
15 whereby the recording medium can be transported in a
good precision. When the recording medium has a warp,
it is effective to add to the roller or the like a
function to correct the warp. If the above mark may
damage the commercial value of products, it may be
20 removed by means of a shearing press or the like after
printing.

A member having the part comprised of aluminum
or an alloy thereof on which the image has been formed
in this way may be used as it is without sealing of
25 the whole pores if it is used, for example, for
interiors. If it is used for exteriors where a

1 reliability is required, the sealing of pores may
preferably be additionally made to form a product.

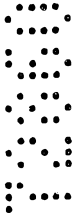
Next, examples of the mechanism in the second
step ink-jet recording used in the process and
5 apparatus of the present invention will be described
below in detail.

In the ink-jet recording on the aluminum
anodic oxide layer, as previously stated, the aluminum
anodic oxide layer itself has no ink permeability and
10 also the pores serving as an ink receptor have not so
large volume. Moreover, there is a limit to
increasing the evaporation of inks. Hence, especially
in the case of a recording process where multi-color
inks are simultaneously shot in plurality, the above
15 process alone may be unsatisfactory in image quality.

Accordingly, the recording is not carried out
all at one time using nozzles arranged in plurality,
but recording scans are divided into several times and
the recording is reciprocally carried out. Use of
20 such a system in combination makes it possible to
obtain high-quality images. Namely, this is a system
in which, when recording is carried out by scanning n-
times, nozzles are arranged in plurality (m-nozzles)
and a printing face is forwarded by m/n , where the
25 printing is repeated to form picture element units of
 $n \times a$, and $n \times a$ picture elements are filled by

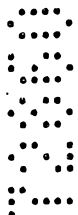
1 scanning divided into n-times. This makes it possible
to eliminate unevenness in recording scans, to gain
time until inks are dyed and fixed, and to keep a
drying time for which ink reception at pores can be
5 completed.

Fig. 10 illustrates a specific example of the
formation of dots on the recording medium of the
present invention. Fig. 10 shows a state in which C-
ink and Y-ink are simultaneously shot in to form dots.
10 Squares shown in the first scan represent the position
of the recording head and the scope in which inks can
be shot in at the scan. The squares painted out in
black are areas in which recording signals have been
actually given to make a record, and the apparatus is
15 so set as for a lower 1/2 part of the head to give a
half shot-in quantity. Next, at the second scan,
paper is forwarded by 1/2 of the nozzle width of the
head to make a record at the remaining area in which
no record has been made at the first scan, using the
upper half of the recording head. Record is carried
20 out also at the lower half in a like pattern to make a
record leaving a 1/2 area unrecorded. This is a
process in which the recording is further repeated for
the third scan and the fourth scan to form a 100%
25 image-recorded area. Here, such a recording process
is called the "two-pass printing".



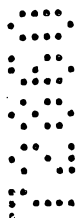
1 This two-pass printing can eliminate the
unevenness for each scan. Since, however, two color
inks are simultaneously shot in as shown in Fig. 10,
the reception quantity of the aluminum anodic oxide
5 layer is required to be doubled. This is unsuitable
for those having a thin aluminum anodic oxide layer as
previously stated. Accordingly, in the case when the
multi-color printing is carried out and in the
recording process in which inks are simultaneously
10 shot in at the same position, it is necessary to
change the pattern for each color to make a record so
that each color ink is shot in at a different position
for each pass.

 Figs. 11A to 11H and 12A to 12H illustrate
15 specific examples in which patterns are changed for
each color to make a record. In the examples shown in
Figs. 11A to 11H and 12A to 12H, Y, M, C and Bk four
color inks are used and recording is carried out using
a recording apparatus as shown in Fig. 13, in which
20 four heads each having 64 nozzles are arranged in
parallel. In Fig. 13, reference numeral 1201 denotes
recording heads corresponding to four colors; 1202, an
ejection orifice; 1203, a carriage; 1204 and 1205,
aluminum sheet feed rollers; 1206, an aluminum sheet
25 having an aluminum anodic oxide layer on its surface;
1207, a rail; and 1208, an encoder.



1 As shown in Figs. 11A to 11H and 12A to 12H,
when four-color recording is carried out, 4x4 picture
elements are arranged so that the four colors do not
overlap one another, and recording signals are
5 selected for each color so that inks are shot in one
pass for four dots among them. Figs. 11A to 11H and
12A to 12H show 16 picture elements in the nozzle
array direction and 16 picture elements in the scan
direction, and the apparatus is so set as to form a
10 100% image-recorded area upon scanning repeatedly
carried out four times. Similar to the example
previously described, the squares painted out in black
are areas in which inks are shot. The aluminum sheet
is forwarded with respect to the heads by 16 nozzles
15 each as a second pass, a third pass and a fourth path
toward the right side to carry out recording. Thus,
inks are not simultaneously shot in for each color,
ink droplets are received in pores within the time the
respective scans are repeated and no bleeding may
20 occur between colors, so that it becomes possible to
form high-quality color images. This recording
process is herein called "color-by-color pass
printing".

 Table 1 shows how the respective printing
25 systems are effective on image quality. Criteria of
judgement on image quality for each system are shown



1 together. "One pass" indicates the recording carried
out by 100% shot-in at usual one scan; "Two passes",
the recording process described above with reference
to Fig. 10; and "Four passes", the recording process
5 described above with reference to Figs. 11A to 11H and
12A to 12H. "Monochrome" indicates an instance where
the recording is carried out in Bk monochrome; and
"Full color", the recording process in which
simultaneous recording is carried out using Y, M, C
10 and Bk four color inks under three-color overlap at
most.

As will be seen from Table 1, in the case of
the monochrome, the scanning line irregularity and the
bleeding on the recording surface are reasonably
15 prevented so long as the recording is divided into at
least two passes, and there is no problem in practical
use. In the case of the full-color printing, high-
quality images can be achieved by four-pass printing
where passes are separated for each color.

20 Table 1

	Monochrome	Full color
One pass:	B	B
Two passes:	A	B
25 Four passes:	AA	AA

1 AA: No bleeding occurs at all and images have a
 good quality.

 A: Bleeding slightly occurs but images are at a
 level not problematic in practical use.

5 B: Bleeding occurs in areas where at least two
 colors are superposed.

 C: Bleeding greatly occurs and images have a very
 poor quality.

 A printing system employing an image forming
10 process according to another embodiment of the present
 invention will be described below.

 In order to increase recording density, it is
 necessary to decrease, on the recording surface, areas
 on which dyes are not fixed. For example, as shown in
15 Figs. 14A and 14B, it is suitable for ink droplets to
 each have a diameter of about 100 μm under recording
 conditions of 360 dpi. Since the distance between the
 centers of ink droplets comes to be 70.5 μm , ink
 droplets 21 form dots in such a way that they overlap
20 with each other on an anodic oxide layer 22 formed on
 an aluminum base 23. Fig. 14A is a top view of
 droplets in Fig. 14B.

 In contrast, if, for example, images are
 recorded at 360 dpi in an ink droplet diameter of 70.5
25 μm , areas having no dyes remain on the surface as
 shown in Figs. 15A and 15B. Fig. 15B is a cross

1 section along the line 15B-15B in Fig. 15A.

When such areas having no dyes remain, no sufficient density can be achieved no matter how high the dye density at each dot is made.

5 Thus, it follows that dots are so formed as to be in the relationship as shown in Figs. 14A and 14B.

However, the anodic oxide layer 22, which is different from paper or recording mediums made up to have an absorptive base material, has no ink
10 permeability, and hence, when a plurality of dots are formed in the state of the ink droplets as shown in Figs. 14A and 14B, the ink having impacted on the surface acts in such a way that the ink droplets come together because of surface tension inherent in the
15 ink.

More specifically, ink droplets standing as shown in Fig. 16A turn into a state as shown in Fig. 16B.

As evaporation of volatile solvents takes
20 place from this state, an ink having increased in dye concentration is left on the surface, and this ink also comes toward the center because of surface tension (Fig. 16C and 16G). With a further progress of this course of action, an image having a dye in a
25 large quantity at the center and in a gradually smaller quantity toward the outside is formed, as



1 shown in Fig. 16D. Also, in some cases, non-volatile
solvents may remain at the center in a concentrated
state.

5 In the case of monochromes, this brings about
an uneven density to lower the quality level of
images. In the case of color images, this may cause
bleeding of inks with different colors adjacently
formed.

10 Figs. 16E and 16F show shapes of ink droplets
21 on the surface of anodic oxide layer 22 of Figs.
16A and 16B, respectively, viewed from the top.

15 In instances in which ink droplets are
superimposingly shot, the volume of ink droplets
increases as shown in Figs. 17A and 17B, to cause ink
run-over, so that even dye-free areas 24 (Fig. 17A)
are colored as shown in Fig. 17B.

20 Figs. 17C and 17D show shapes of ink droplets
21 on the surface of anodic oxide layer 22 of Figs.
17A and 17B, respectively, viewed from the top.

25 Now, in the present invention, as shown in
Figs. 18A to 18F and Figs. 19A to 19F, after volatile
solvents of ink droplets having impacted first have
substantially evaporated (Figs. 18A to 18C), the next
ink droplets are made to impact (Figs. 18A to 18C).
Thus, neither uneven density nor bleeding as stated
above may occur.

1 Figs. 18G through 18L show shapes of dots and ink droplets on the surface of anodic oxide layer of Figs. 18A through 18F, respectively, viewed from the top.

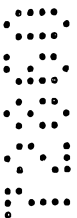
5 This can be accomplished by recording dot-interval images several times as shown in Fig. 20.

More specifically, at first-pass printing, nozzles N1 and N3 are simultaneously driven to print odd-numbered lines; at second-pass printing, nozzles
10 N2 and N4 are simultaneously driven to print even-numbered lines; at third-pass printing, nozzles N2 and N4 are simultaneously driven to print odd-numbered lines; and at fourth-pass printing, nozzles N1 and N3 are simultaneously driven to print even-numbered
15 lines.

Thus, dots in the same pass become distant by two dots (DB in the drawing) and hence it becomes possible to prevent any bleeding caused by dots in the same pass and between passes.

20 In the case of color images, this procedure may be similarly repeated so that a first color is fixed and thereafter the next color is fixed.

In this case, in order to prevent misregistration between colors, multi-color
25 registration may be carried out by a mechanical means or electrical means known in the art.



1

EXAMPLES

The present invention will be described below in greater detail by giving Examples.

Example 1

5

On the surfaces of A4 size aluminum sheets (sheet thickness: 0.5 mm) on which aluminum anodic oxide layers of about 10 μ m thick each had been formed, images were formed along the steps according to the process of the present invention, using the recording apparatus as previously described and also using inks.

10

In the first step and the third step, heating and drying were employed, and were carried out under conditions as shown in Table 2 below, i.e., appropriate combination with no heating, heating at 40°C or heating at 60°C. Image quality was evaluated on the recorded images obtained. Criteria and results of the evaluation are shown together in Table 2. As is seen from the results shown in Table 2, good images can be finally obtained when the heating at 60°C is applied in the first treatment step and the heating at 40°C or above is applied in the third treatment step. As is also seen therefrom, no good images can be formed even though the third treatment steps are carried out under any conditions, when the first treatment step is omitted.

15

20

25

1 Table 2

		Third step		
		No heating	40°C	60°C
5	<u>First step</u>			
	No heating:	C	C	C
	40°C:	C	B	A
	60°C:	B	AA	AA

- 10 AA: No bleeding occurs at all and images have a good quality.
- A: Bleeding slightly occurs but images are at a level not problematic in practical use.
- 15 B: Bleeding occurs in areas where at least two colors are superposed.
- C: Bleeding greatly occurs and images have a very poor quality.

Example 2

- 20 Influences of the solvent proportion of non-volatile component in ink when the ink-jet recording was carried out on the aluminum anodic oxide layer according to the present invention were examined using glycerol as the solvent, to make evaluation as
- 25 reported below.

Using 100 g of ink solutions prepared by

1 mixing 3 g of a dye, glycerol in the amount as shown
in Table 3 below and the balance of water and IPA in a
ratio of 10:1, bubble-jet type ink-jet recording was
carried out along the steps according to the process
5 of the present invention, on aluminum sheets (A) on
which anodic oxide layers (aluminum anodic oxide
layers) with a layer thickness of 10 μm each had been
formed and aluminum sheets (B) on which anodic oxide
layers (aluminum anodic oxide layers) with a layer
10 thickness of 20 μm each had been formed.

Image quality was evaluated on the recorded
images obtained. Criteria of the evaluation are the
same as those in Example 1. Results obtained are
shown together in Table 3. As is seen from the
15 results shown in Table 3, in the case of the aluminum
sheet having an aluminum anodic oxide layer with a
layer thickness of 10 μm , a good image quality is
attained when the glycerol is in a percentage of 5% or
less. In the case of the aluminum sheet having an
20 aluminum anodic oxide layer with a layer thickness of
20 μm , a better image quality is attained when the
glycerol is in a percentage of 10% or less.

Table 3

1

Amount of glycerol (g)	A 10μm thick layer	B 20μm thick layer
5	1 AA	AA
	3 AA	AA
	5 A	AA
	10 -	A

10

Example 3

On aluminum sheets with a sheet thickness of 0.5 mm on which aluminum anodic oxide layers of about 20 μm thick each had been formed, which were subjected to dehydration and activation treatments, images were formed by bubble jet recording, using an ink composed of the following.

15

C.I. Direct Black 168	3% by weight
Ethylene glycol	10% by weight
Isopropyl alcohol	5% by weight
Water	82% by weight.

20

Next, the aluminum sheets on which images were thus formed were washed with an aqueous 10% by weight $AlCl_3$ solution for 3 minutes, followed by further washing with water for 5 minutes.

25

Samples thus washed and samples having been not washed were tested for their 50 hour light-fastness by the use of a fade-O-meter (ATLAS Ci35).

1 Evaluation was made using a reflection
densitometer (MACBETH R-D915), where reflection
densities were measured before the light-fastness test
and after the light-fastness test to compare the
5 retensions.

$$\text{Retension} = \frac{\text{Reflection density after light-fastness test}}{\text{Reflection density before light-fastness test}} \times 100$$

Results obtained are shown in Table 4.

The washing with an aqueous polyvalent metal
10 salt solution is seen to bring about an improvement in
light-fastness.

Table 4

	Washed	Not washed
15 Retension of reflection density:	80% or more	Less than 80%

Example 4

20 On 0.5 mm thick aluminum sheets on which
aluminum anodic oxide layers of 20 μm thick each had
been formed, images were formed by bubble jet
recording as in Example 3, using the same ink as used
in Example 3.

25 Next, samples were prepared, some of which
were subjected to sealing of pores of anodic oxide

1 layers by the use of an aqueous 1% by weight AlCl_3
solution, and some of which were not.

Evaluation was made in the same manner as in
Example 3.

5 Results obtained are shown in Table 5.

The sealing of anodic oxide layers by the use
of an aqueous polyvalent metal salt solution is seen
to bring about an improvement in light-fastness.

Table 5

10

	Sealed	Not sealed
Retension of reflection density:	85% or more	Less than 80%

15 As described above, according to the image
forming process of ^{this embodiment,} ~~the present invention,~~ the
reactivity with dyes and the ink reception quantity
are improved when the anodic oxide layer formed on the
20 surface of a plate, sheet or foil of aluminum or an
alloy thereof is subjected to the dehydration and
activation treatments before the ink droplets are
imparted thereto. Also, recorded images having a
superior image performance can be finally formed on
25 the anodic oxide layer when, after the ink droplets
have been imparted, the volatile components in inks



1 mixedly present in the layer are evaporated to fix the
dyes (coloring matter) in the inks on the layer to
thereby improve ink fixing performance.

According to the apparatus of ^{this embodiment,}
~~the present~~

5 ~~invention,~~ recorded images having a superior image
performance can be finally formed on the anodic oxide
layer provided on the surface of a plate, sheet or
foil of aluminum or an alloy thereof, according to the
process as described above.

10 The decorative aluminum plate, sheet or foil
of the present invention has been treated and
processed in the manner as described above, before the
recorded images are formed, i.e., before inks are
imparted to the anodic oxide layer provided on the
15 surface of a plate, sheet or foil of aluminum or an
alloy thereof, and hence has a superior image
performance.

According to ^{this embodiment,}
~~the present invention,~~ images and
decorative aluminum sheets having a superior light-
20 fastness can be formed when, after recorded images
have been formed, the aqueous polyvalent metal salt
solution is applied to the anodic oxide layer formed
on the surface of a plate, sheet or foil of aluminum
or an alloy thereof.

25 According to ^{this embodiment,}
~~the present invention,~~ the
coloring ability of ink can be improved when the



1 anodic oxide layer formed on the surface of a plate,
sheet or foil of aluminum or an alloy thereof is
subjected to the dehydration and activation treatments
before the ink droplets are imparted thereto. Also,
5 in the recording carried out plural times by imparting
ink droplets so as to form dot-interval images, in the
case when the next ink droplets are imparted
adjacently to the ink droplets first imparted, the
next ink droplets are imparted to the adjacent areas
10 after the ink at least in the areas where they are
superimposed on the ink droplets first imparted has
been substantially fixed and the dye in the ink has
been also fixed. In the case when the next ink
droplets are imparted superimposingly to the ink
15 droplets first imparted, the next ink droplets are
superimposed after the ink droplets first imparted has
been substantially fixed and the dye in the ink has
been also fixed. This makes it possible to form
images free of ink bleeding and to finally form
20 recorded images having a superior image performance on
the anodic oxide layer, and decorative aluminum sheets
having such recorded images.

The claims defining the invention are as follows:

1. An image forming process for forming an image on an anodic oxide layer formed on the surface of a plate, sheet or
5 foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink containing a dye and a volatile component, comprising the steps of:
heating the anodic oxide layer to dehydrate and
activate the anodic oxide layer;
10 imparting ink to the anodic oxide layer having been subjected to heat treatment; and
removing the volatile component from the ink imparted and fix the dye into the anodic oxide layer.
- 15 2. The image forming process according to claim 1, further comprising a step of sealing pores in the anodic oxide layer after fixing the dye into the anodic oxide layer.
- 20 3. The image forming process according to claim 1, wherein the ink comprises multi-color inks to form a multi-colored printed image.
- 25 4. The image forming process according to claim 1, wherein the anodic oxide layer has a thickness of from 5 to 25 μm .
5. The image forming process according to claim 1, wherein the ink-jet printing is a bubble-jet printing.
- 30 6. The image forming process according to claim 1, wherein the volatile component of the ink has an evaporation rate of from $1.0 \times 10^{-5} \text{ g/mm}^2 \cdot \text{sec}$ to $1.0 \times 10^{-7} \text{ g/mm}^2 \cdot \text{sec}$.
7. The image forming process according to claim 1,
35 further comprising a step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer after ink has been applied.



8. The image forming process according to claim 1, wherein the volatile component-removing step includes treating the anodic oxide layer with heat.

5 9. The image forming process according to claim 1, wherein said ink further comprises a non-volatile component and the amount per unit area of the non-volatile component imparted to the anodic oxide layer is not more than ink reception quantity per unit area of pores in the anodic oxide layer.

10

10. A process for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing
15 process with an ink containing a dye and a volatile component, comprising the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;

imparting ink to the anodic oxide layer having been
20 subjected to heat treatment; and

removing the volatile component from the ink imparted and fix the dye contained in the ink into the anodic oxide layer.

25

11. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, further comprising a step of sealing pores in the anodic oxide layer after fixing the dye into the anodic oxide layer.

30

12. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein the ink comprises multi-color inks to form a multi-colored printed image.

35

13. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein the anodic oxide layer has a thickness of from 5 to 25 μm .



14. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein the ink-jet printing is a bubble-jet printing.

5 15. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein the volatile component of the ink has an evaporation rate of from 1.0×10^{-5} g/mm²·sec to 1.0×10^{-7} g/mm²·sec.

10 16. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, further comprising a step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer after ink has been applied.

15 17. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein the volatile component-removing step includes treating the anodic oxide layer with heat.

20 18. The process for producing a decorative aluminum plate, sheet or foil according to claim 10, wherein said ink further comprises a non-volatile component and the amount per unit area of the non-volatile component imparted to the anodic oxide layer is not more than ink reception quantity per unit
25 area of pores in the anodic oxide layer.

19. An apparatus for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer formed on the surface of a plate, sheet or foil made of
30 aluminum or an aluminum alloy, comprising:

a first means for heating the aluminum plate, sheet or foil to dehydrate and activate the anodic oxide layer;

a printing head provided adjacent to the first means, having a plurality of ink ejection orifices from which ink is
35 applied to the anodic oxide layer in accordance with image printing signal, wherein ink comprises a dye and a volatile component;

a second means for heating the aluminum plate, sheet



or foil to remove the volatile component from the ink applied and fix the dye contained in the ink in the anodic oxide layer; and

a third means for transporting the aluminum plate,
5 sheet or foil from the first means to the second means.

20. The apparatus according to claim 19, further comprising a means for detecting the temperature of the aluminum plate, sheet or foil and a means for controlling at
10 least one operation of the first heating means and the second heating means in accordance with the information on the temperature obtained in the temperature detecting means.

21. The apparatus according to claim 19, wherein the
15 transporting means comprises a tray on which the aluminum plate, sheet or foil is put.

22. The apparatus according to claim 21, wherein the tray comprises a means for heating the aluminum plate, sheet or
20 foil.

23. The apparatus according to claim 19, wherein the printing head is an ink-jet printing head.

24. The apparatus according to claim 23, wherein the ink-jet printing head is a bubble jet printing head.

25. An image forming process for forming an image on an anodic oxide layer formed on the surface of a plate, sheet or
30 foil made of aluminum or an aluminum alloy, using an ink-jet printing process with an ink containing a dye and a volatile component, comprising the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;
35 imparting ink to the anodic oxide layer having been subjected to heat treatment by performing dot-interval printing by scanning a printing head plural times; and removing a volatile component contained in the ink



from the anodic oxide layer to fix the dye contained in the ink into the anodic oxide layer.

26. The image forming process according to claim 25,
5 wherein, during the ink-imparting step, said dot-interval printing is performed in such a manner that the dots printed in one dot-interval printing do not become continuous on the anodic oxide layer.

10 27. The image forming process according to claim 25, wherein during the ink-imparting step, ink droplets from a second scan of the printing head are imparted adjacently to ink droplets from a first scan of the printing head after the volatile component in the ink droplets from the first scan has
15 evaporated.

28. The image forming process according to claim 25, wherein during the ink-imparting step, ink droplets from a second scan of the printing head are superimposed on ink
20 droplets from a first scan of the printing head after the volatile component in the ink droplets from the first scan has evaporated.

29. The image forming process according to claim 25,
25 wherein said ink comprises multi-color inks to form a multi-colored printed image.

30. The image forming process according to claim 25, wherein treatment in the volatile component-removing step
30 includes treating the anodic oxide layer with heat.

31. The image forming process according to claim 25, wherein the volatile component-removing step includes treating the anodic oxide layer by electromagnetic induction.

35

32. The image forming process according to claim 25, wherein the volatile component-removing step includes treating the anodic oxide layer by dry-air blowing.



33. The image forming process according to claim 25, further comprising a fourth step of sealing pores in the anodic oxide layer after fixing the dye into the anodic oxide layer.

5 34. The image forming process according to claim 25, said ink-jet printing process is a bubble jet printing process.

35. The image forming process according to claim 25, further comprising a step of applying an aqueous polyvalent
10 metal salt solution to the anodic oxide layer after ink has been applied.

36. The image forming process according to claim 25, wherein the anodic oxide layer has a thickness of from 5 to 25
15 μm .

37. The image forming process according to claim 25, wherein said ink further comprises a non-volatile component and the amount per unit area of the non-volatile component imparted
20 to the anodic oxide layer is not more than ink reception quantity per unit area of pores in the anodic oxide layer.

38. A process for producing a decorative aluminum plate, sheet or foil having an image printed on an anodic oxide layer
25 formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, using an ink-jet printing process, comprising the steps of:

heating the anodic oxide layer to dehydrate and activate the anodic oxide layer;

30 imparting ink to the anodic oxide layer having been subjected to heat treatment by performing dot-interval printing by scanning a printing head plural times; and

removing a volatile component contained in the ink from the anodic oxide layer to fix a dye contained in the ink
35 into the anodic oxide layer.

39. The process for producing a decorative aluminum



plate, sheet or foil according to claim 38, wherein, during the ink-imparting step, the dot-interval printing is performed such that the dots printed in one dot-interval printing are not continuous on the anodic oxide layer.

5

40. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein, during the ink-imparting step, ink is imparted during a second scan of the printing head adjacent to ink imparted during a first scan of the printing head after a volatile component in the ink from the first scan has evaporated.

41. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein, during the ink-imparting step, ink is imparted during a second scan of the printing head superimposed on ink imparted during a first scan of the printing head after the volatile component in the ink from the first scan has evaporated.

42. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein the ink comprises multi-color inks to form a multi-colored printed image.

43. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein the volatile component-removing step includes treating the anodic oxide layer with heat.

44. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein the volatile component-removing step includes treating the anodic oxide layer by electromagnetic induction.

45. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein the volatile component-removing step includes a step of blowing dry-air across the anodic oxide layer.



46. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, further comprising a fourth step of sealing pores in the anodic oxide layer after fixing the dye into the anodic oxide layer.

5

47. The process for producing a decorative aluminum plate, sheet or foil according to a claim 38, wherein the ink-jet printing process is a bubble printing process.

10 48. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, further comprising a step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer after ink has been applied.

15 49. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein the anodic oxide layer has a thickness of from 5 to 25 μm .

20 50. The process for producing a decorative aluminum plate, sheet or foil according to claim 38, wherein said ink further comprises a non-volatile component and the amount per unit area of the non-volatile component imparted to the anodic oxide layer is not more than ink reception quantity per unit area of pores in the anodic oxide layer.

25

51. An image forming process, substantially as herein described with reference to Fig. 7.

30 52. An image forming process, substantially as herein described with reference to Fig. 13.

53. An apparatus, substantially as herein described with reference to Fig. 7.



54. An apparatus, substantially as herein described with reference to Fig.
13.

DATED this Twenty-ninth Day of October 1997

Canon Kabushiki Kaisha

Patent Attorneys for the Applicant

SPRUSON & FERGUSON

5

2000

1000



Image Forming Method, Process for Producing Decorative Aluminum Plate, Apparatus for Carrying out the Process, Decorative Aluminum Plate, and Recording Medium

Abstract

- 5 The invention provides an image forming process for the formation of a recorded image by imparting ink droplets of at least one colour from a recording head (710) having a plurality of ink ejection orifices to an anodic oxide layer formed on the surface of a plate, sheet or foil made of aluminum or an aluminum alloy, comprising:
- a first step of dehydrating and activating said anodic oxide layer;
- 10 a second step for the formation of a recorded image by causing the ink droplets to fly from the ejection orifices in accordance with image recording signals and applying the ink droplets to a desired position of the anodic oxide layer thus dehydrated and activated; and
- a third step of fixing a dye contained in the ink droplets having adhered to the
- 15 anodic oxide layer on which said recorded image has been formed, into said anodic oxide layer, and removing volatile components contained in said ink droplets from said anodic oxide layer.

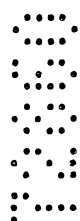


Figure 7

FIG. 1

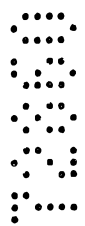
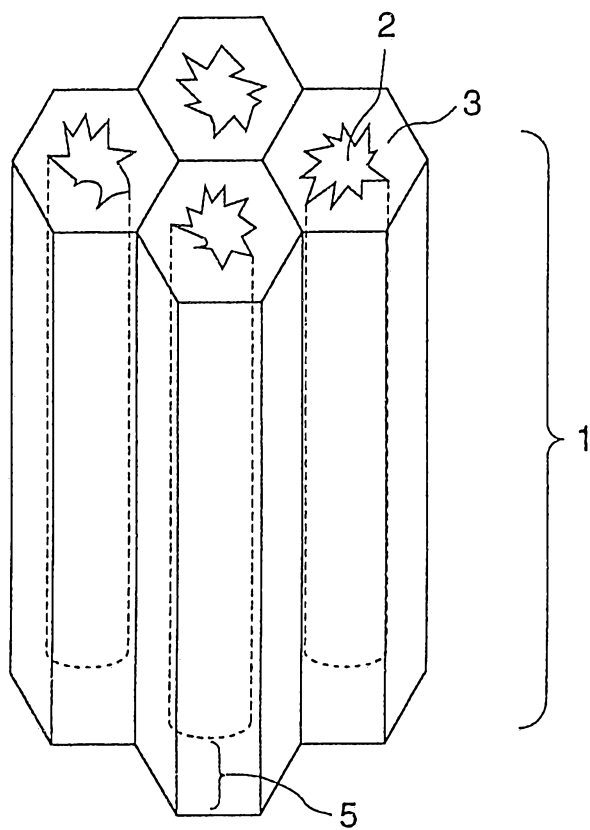


FIG. 2A

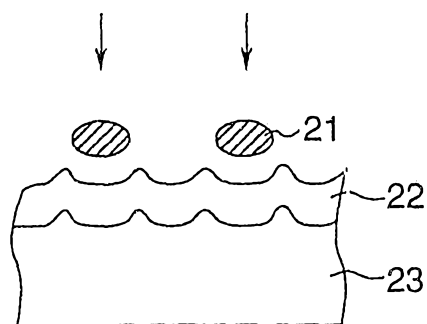


FIG. 2D

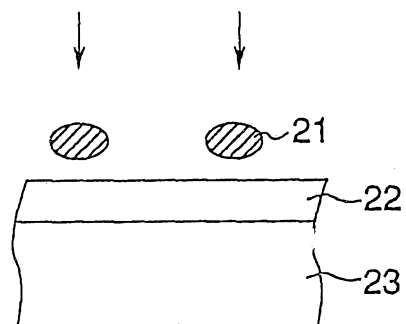


FIG. 2B

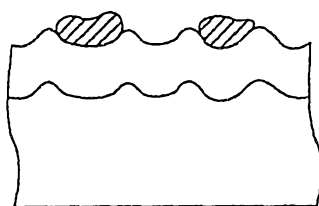


FIG. 2E

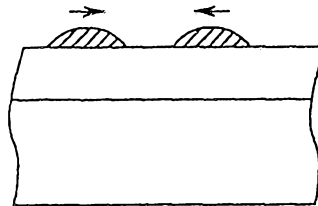


FIG. 2C

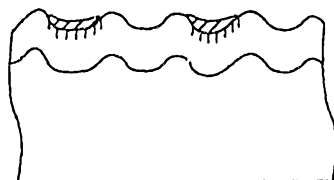


FIG. 2F

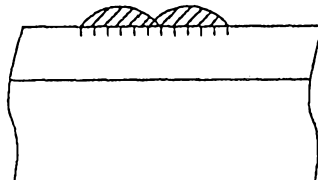


FIG. 3

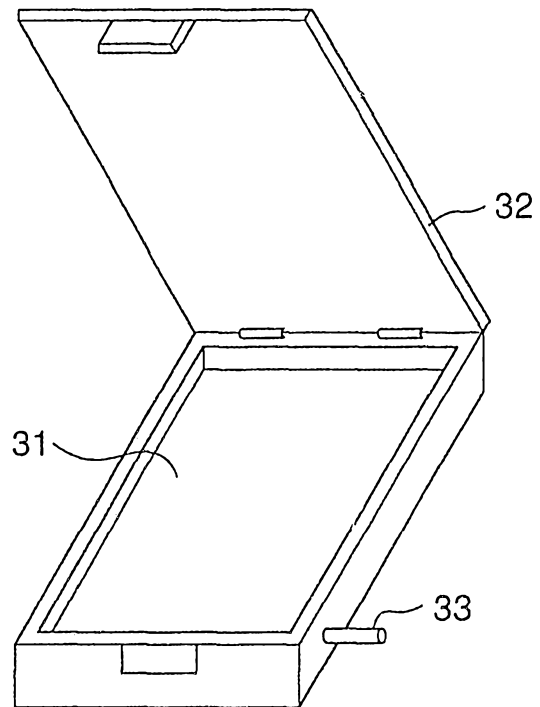


FIG. 4

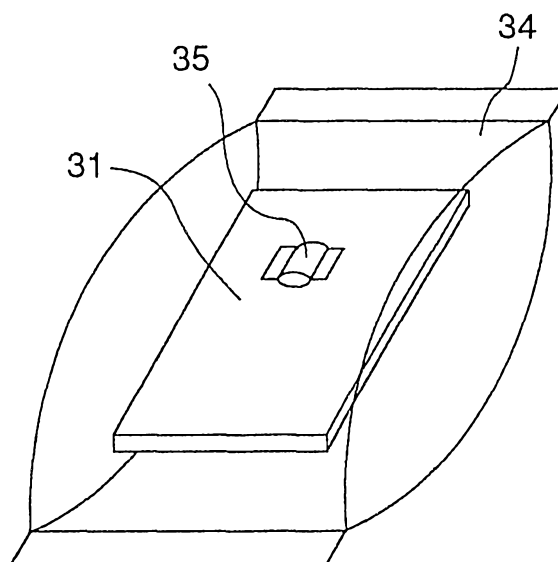


FIG. 5

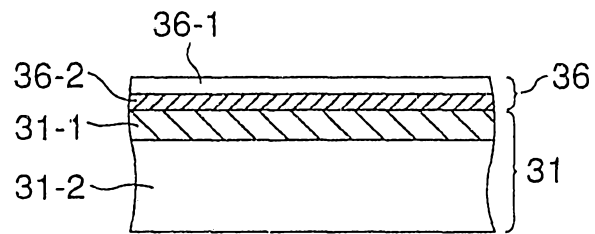
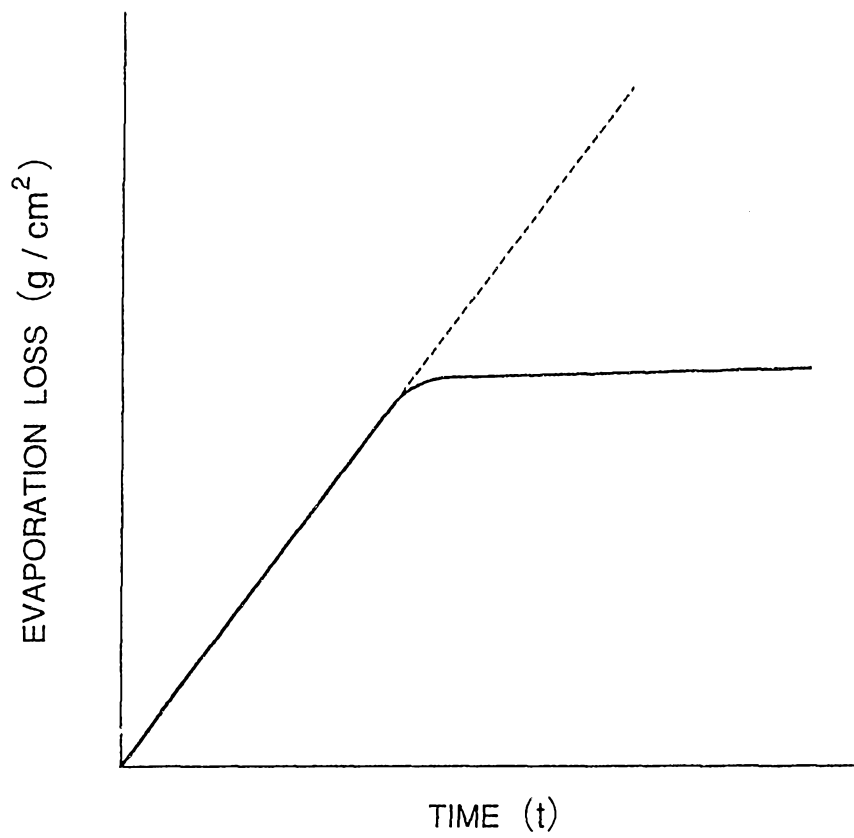
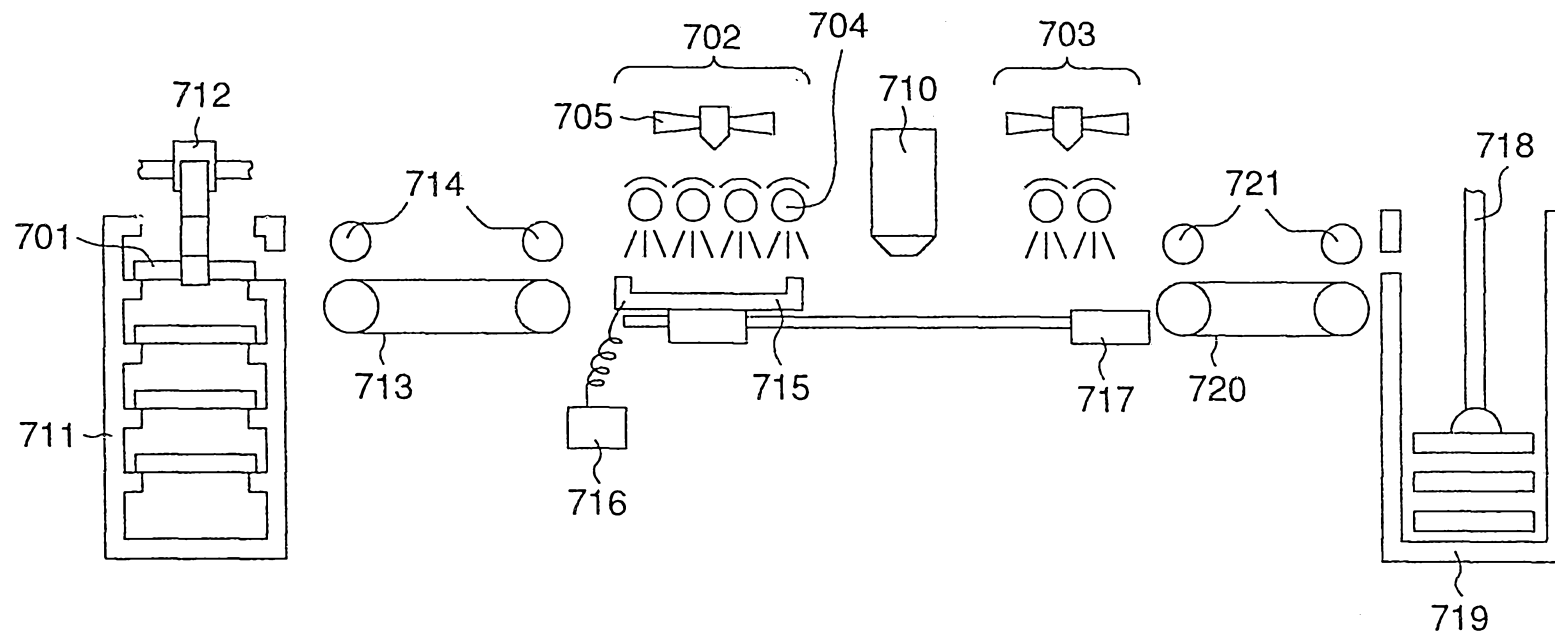


FIG. 6



09 09 94 72000

FIG. 7



72860/94

FIG. 8

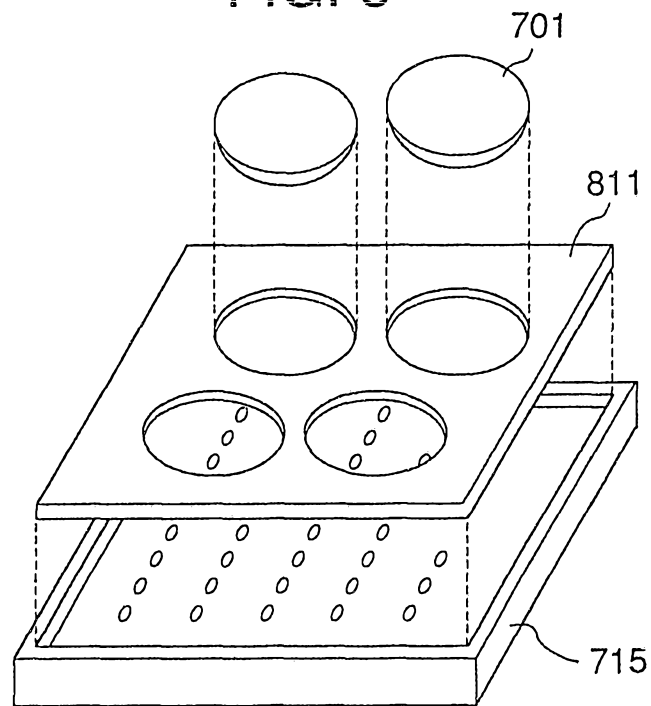
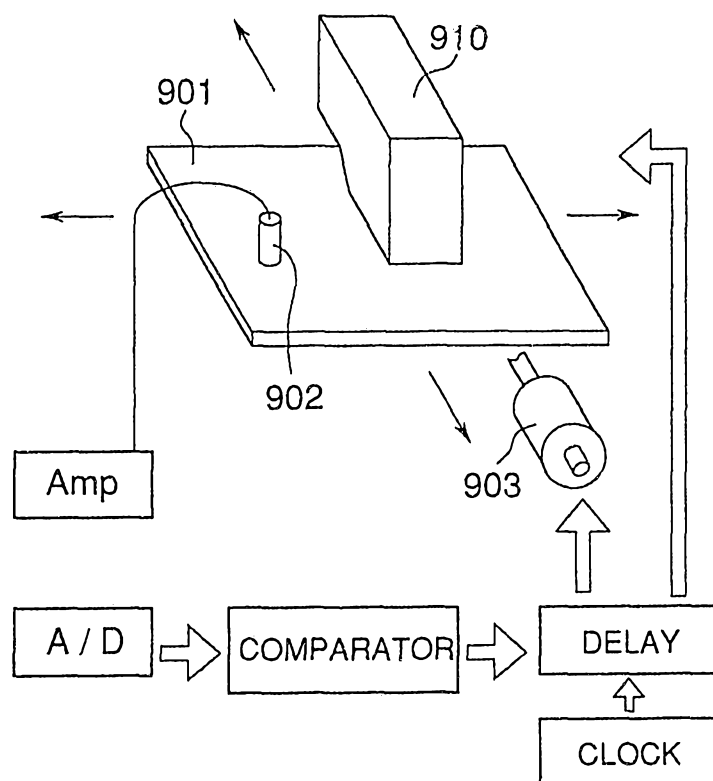
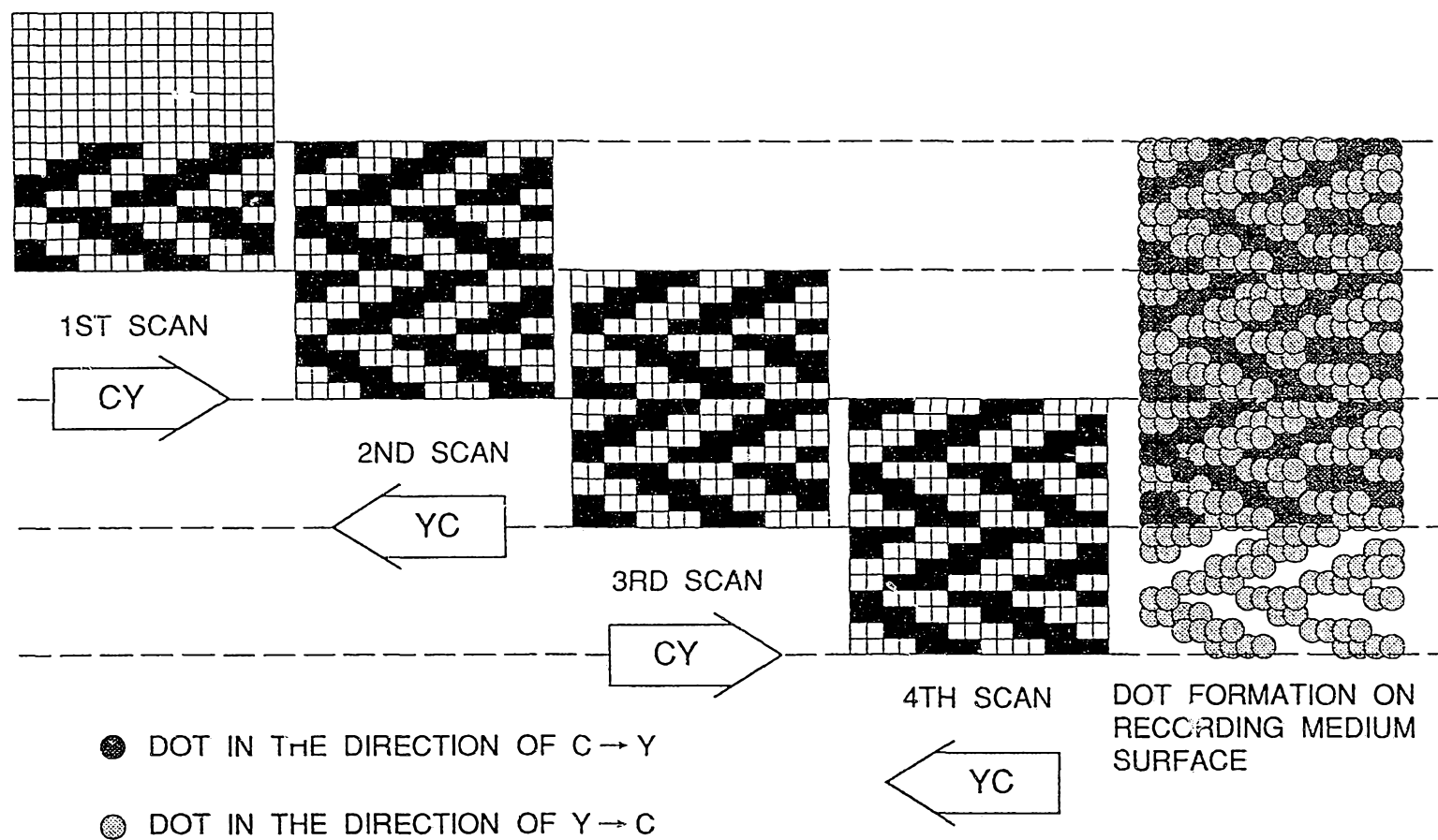


FIG. 9



00 00 94 72000

FIG. 10



72860/94

09 09 94 72860

FIG. 11A

1st-pass

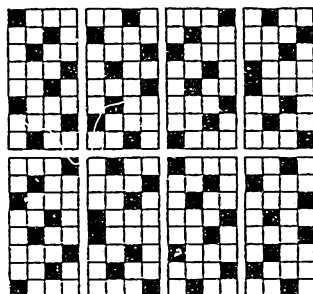


FIG. 11B

2nd-pass

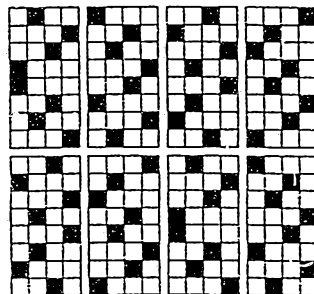


FIG. 11C

3rd-pass

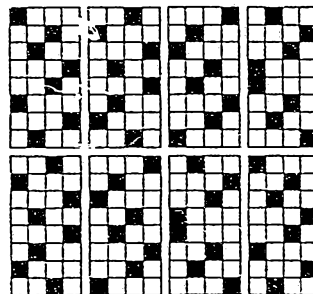
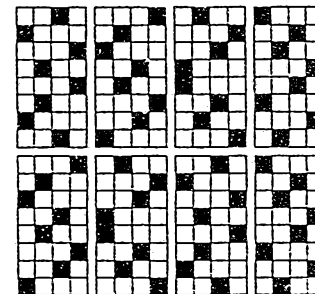


FIG. 11D

4th-pass



Bk

FIG. 11E

1st-pass

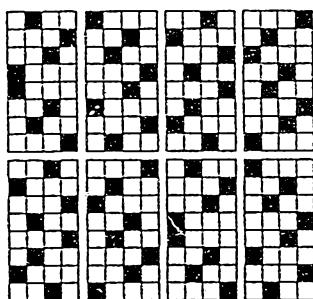


FIG. 11F

2nd-pass

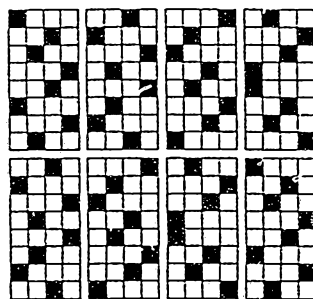


FIG. 11G

3rd-pass

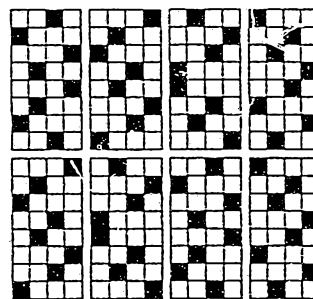
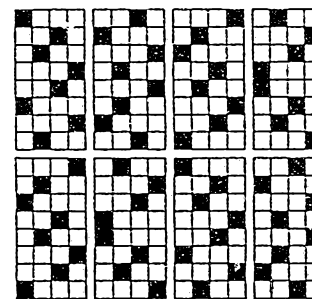


FIG. 11H

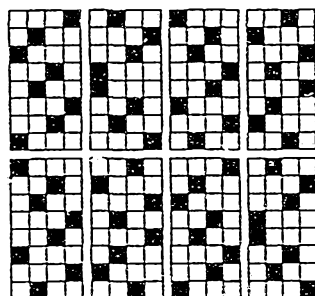
4th-pass



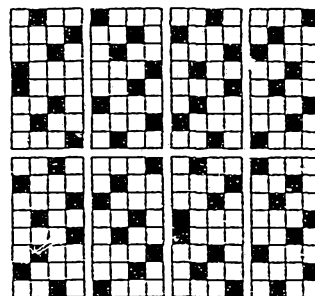
C

M

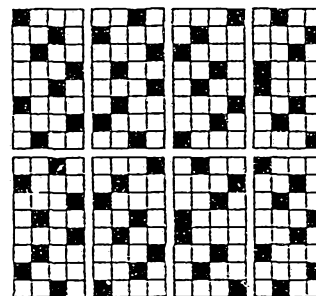
1st-pass



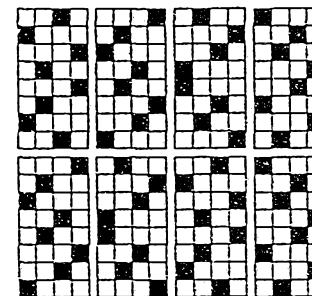
2nd-pass



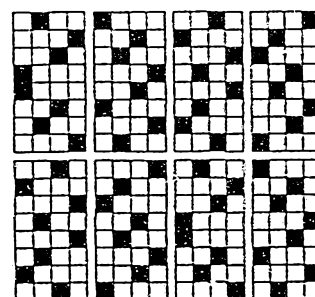
3rd-pass



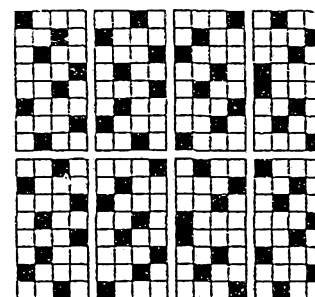
4th-pass



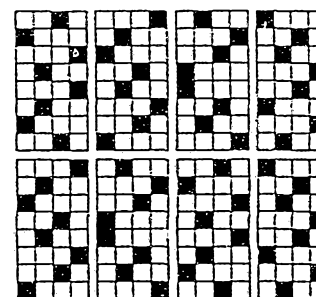
1st-pass



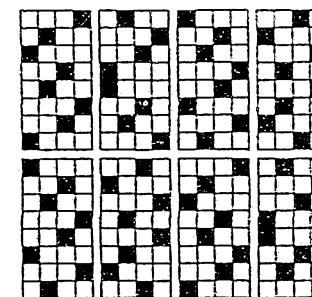
2nd-pass



3rd-pass



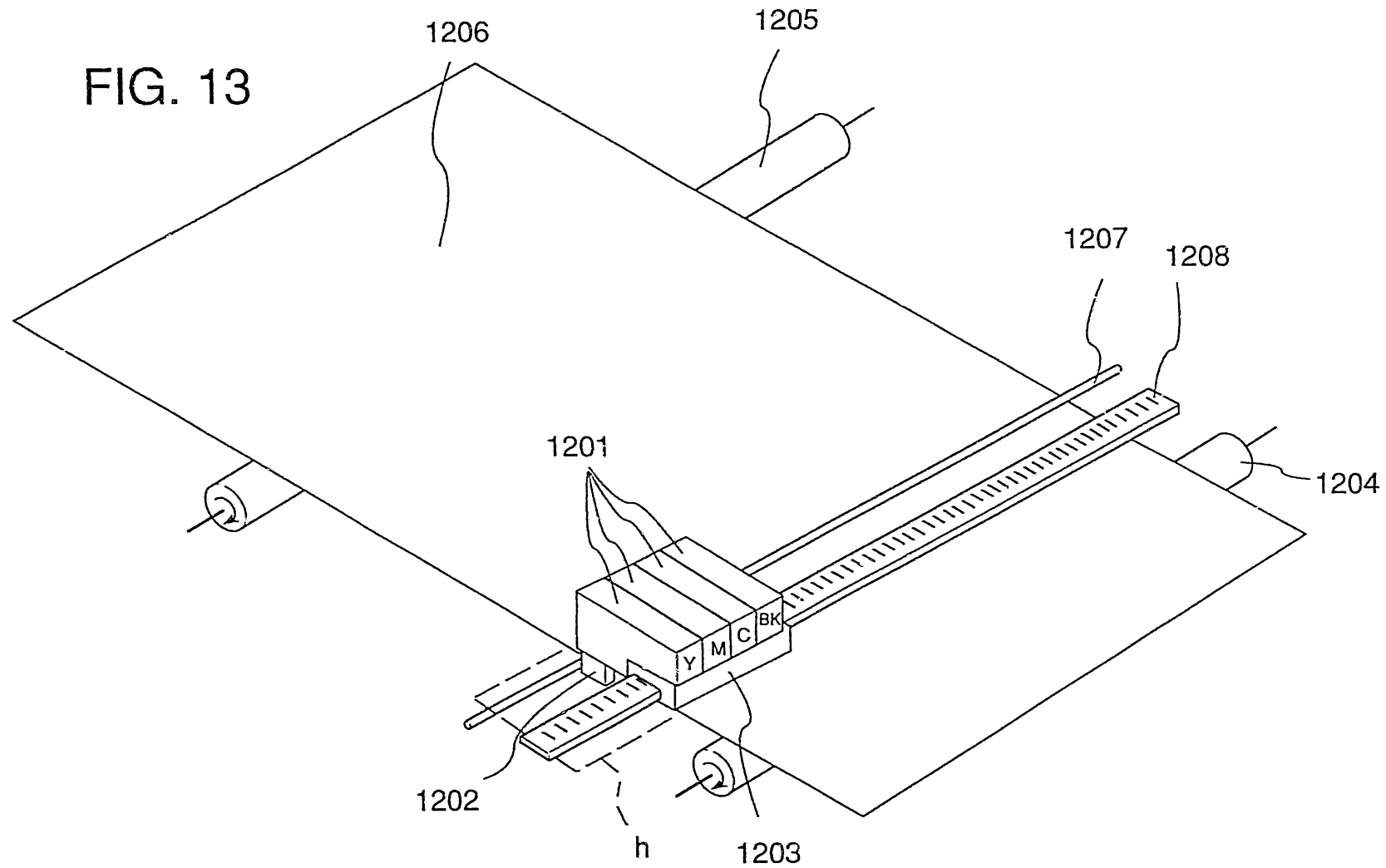
4th-pass



Y

09 09 94 72860

FIG. 13



72860/94

FIG. 14A

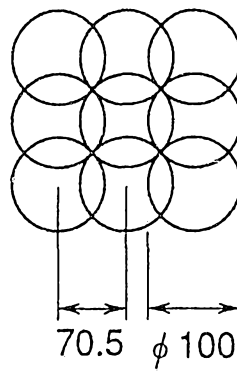


FIG. 14B

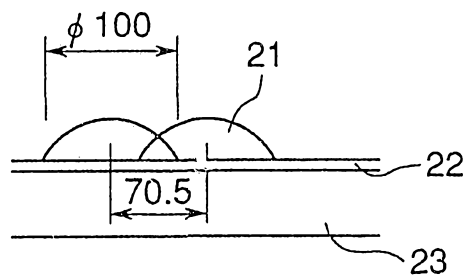


FIG. 15A

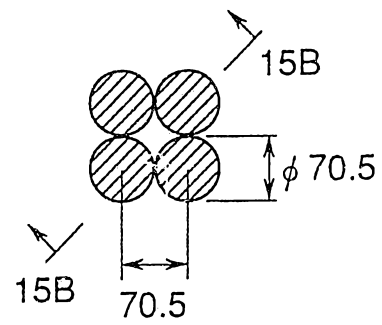


FIG. 15B

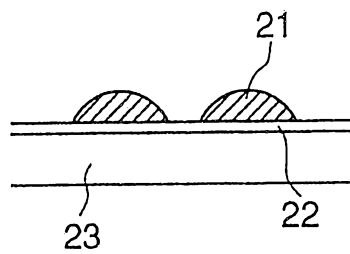


FIG. 16A

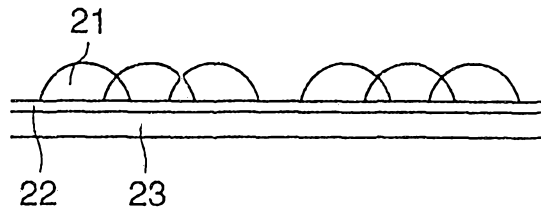


FIG. 16E

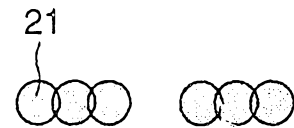


FIG. 16B

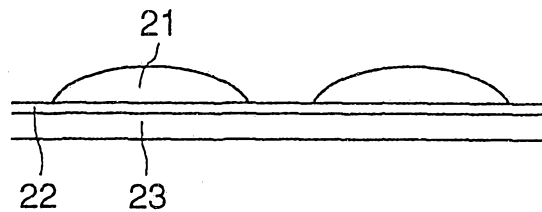


FIG. 16F



FIG. 16C

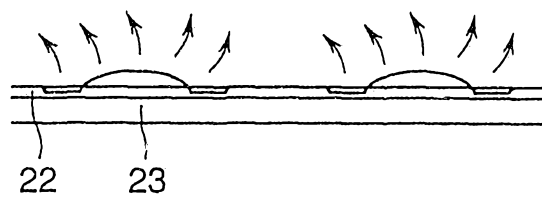


FIG. 16G



FIG. 16D

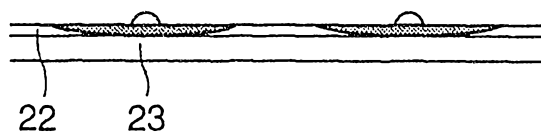


FIG. 17A

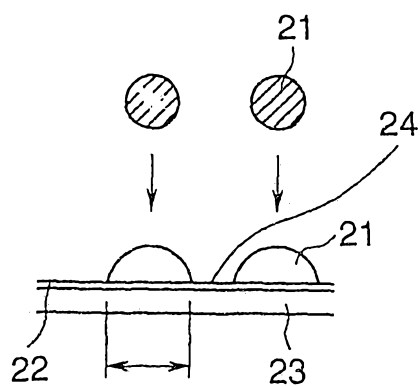


FIG. 17C



FIG. 17B

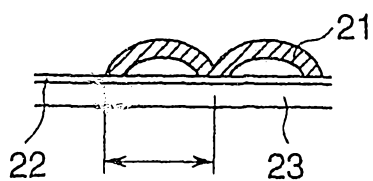


FIG. 17D

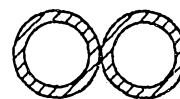


FIG. 18A

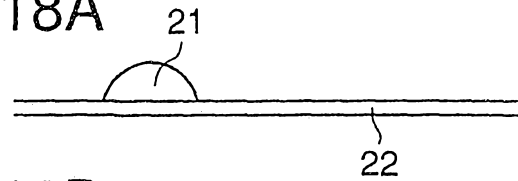


FIG. 18B



FIG. 18C

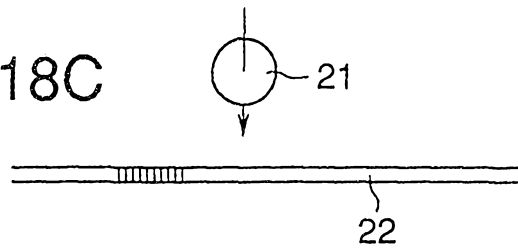


FIG. 18D



FIG. 18E

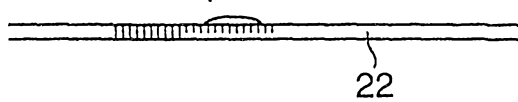


FIG. 18F

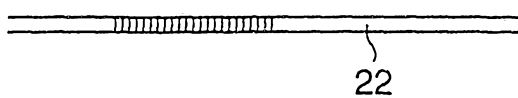


FIG. 18G



FIG. 18H



FIG. 18I



FIG. 18J



FIG. 18K



FIG. 18L



FIG. 19A

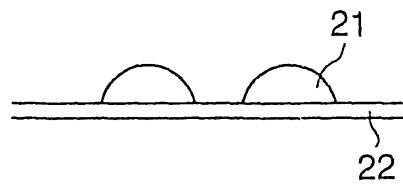


FIG. 19B

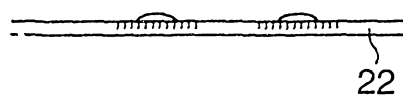


FIG. 19C

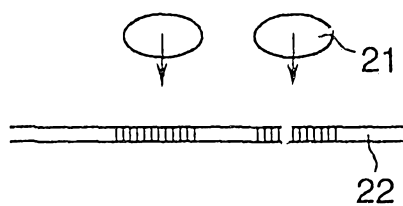


FIG. 19D

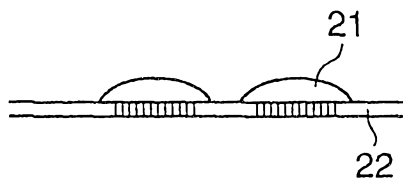


FIG. 19E



FIG. 19F

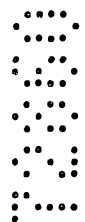
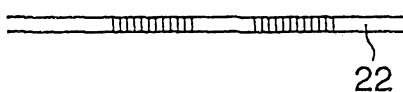


FIG. 20

