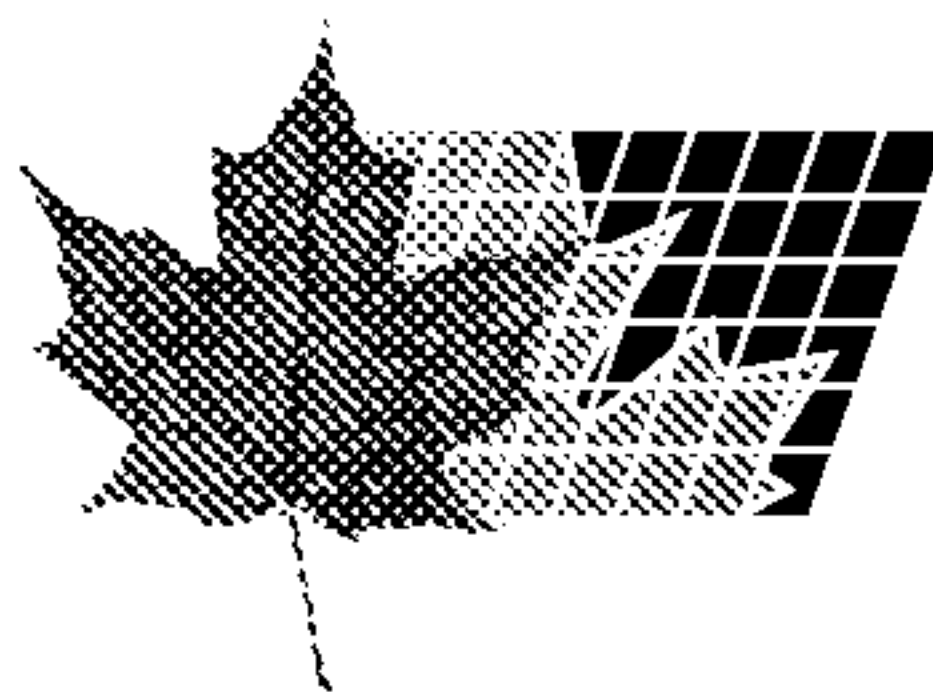




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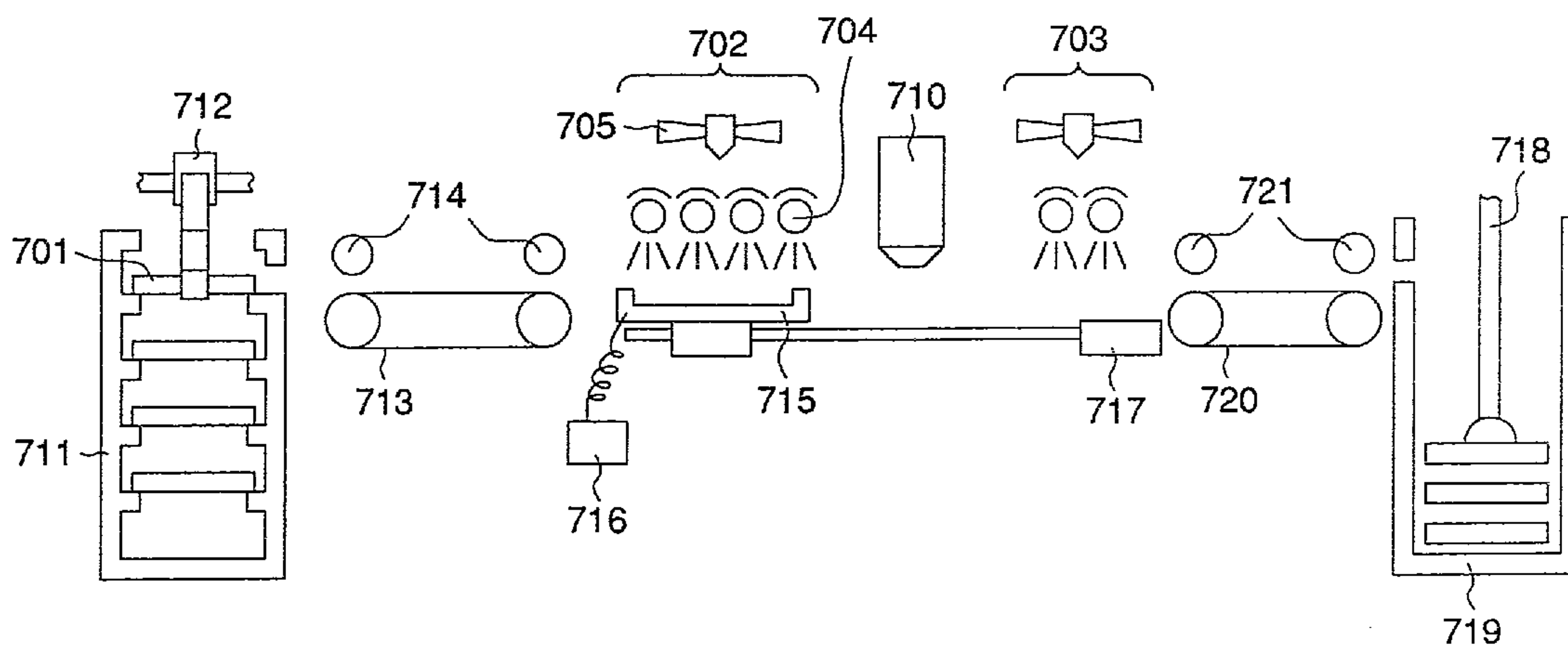
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(54) **METHODE DE PRODUCTION D'IMAGES, PROCEDE DE PRODUCTION DE PLAQUES D'ALUMINIUM DECORATIVES, APPAREIL UTILISANT CE PROCEDE, PLAQUES D'ALUMINIUM DECORATIVES ET SUPPORT D'ENREGISTREMENT CONNEXE**

(54) **IMAGE FORMING METHOD, PROCESS FOR PRODUCING DECORATIVE ALUMINUM PLATE, APPARATUS FOR CARRYING OUT THE PROCESS, DECORATIVE ALUMINUM PLATE, AND RECORDING MEDIUM**



(57) Before ink-jet recording, an image forming surface comprising an anodic oxide layer of aluminum or an alloy thereof is dried and activated. After the recording, a treatment to remove solvent components of ink and fix a dye in the ink is applied.

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1 ABSTRACT OF THE DISCLOSURE

Before ink-jet recording, an image forming  
surface comprising an anodic oxide layer of aluminum  
or an alloy thereof is dried and activated. After the  
5 recording, a treatment to remove solvent components of  
ink and fix a dye in the ink is applied.

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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.

- 1     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.

5

#### SUMMARY OF THE INVENTION

      The present invention has been made taking  
account of these problems, and intends to provide an  
image forming process, a process for producing a  
10 decorative aluminum sheet and an apparatus for its  
production that are necessary for a technique in which  
an ink-jet recording system is employed to form on  
anodic oxide layers, images having a superior image  
performance, e.g., free of color mixture, uneven scans  
15 and crushed images and having a sufficient color  
density. The present invention also intends to  
provide a decorative aluminum sheet having a superior  
image performance, formed by such a technique.

      The image forming process for producing a  
20 decorative aluminum plate, sheet or foil according to  
the present invention that can achieve the above  
objects is an ink-jet recording process for forming a  
recorded image by imparting ink droplets of at least  
one color from a recording head having a plurality of  
25 ink ejection orifices to an anodic oxide layer formed  
on the surface of a plate, sheet or foil made of

1 aluminum or an aluminum alloy, the process comprising;  
a first step of dehydrating and activating the  
anodic oxide layer;  
a second step for the formation of a recorded  
5 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  
10 a third step of fixing a dye contained in the  
ink droplets having adhered to the anodic oxide layer  
on which the recorded image has been formed, into the  
anodic oxide layer, and removing volatile components  
contained in the ink droplets from the anodic oxide  
15 layer.

In the process of the present invention, multi-  
color inks are preferably used as the ink so that a  
colored recorded image can be formed. In the process  
of the present invention, each treatment applied to  
20 the anodic oxide layer in at least one of the first  
step and the third step is carried out by a treatment  
selected from a treatment of heating the layer, a  
treatment by electromagnetic induction and a treatment  
by dry-air spraying. Two or more treatments of these  
25 may be used in combination. The third step may also  
comprise a treatment by rinsing with water.

1                   In the process of the present invention, the  
second step may preferably be carried out by bubble  
jet recording system.

                  As for the apparatus for producing a  
5   decorative aluminum plate, sheet or foil according to  
the present invention, it is an apparatus for forming  
a recorded image on a recording medium having an  
anodic oxide layer formed on the surface of a plate,  
sheet or foil made of aluminum or an aluminum alloy,  
10 by imparting ink droplets of at least one color to the  
anodic oxide layer formed thereon, the apparatus  
comprising;

                  (a) a means for dehydrating and activating the  
anodic oxide layer;

15                  (b) a recording head having a plurality of ink  
ejection orifices from which the ink droplets are  
caused to fly in accordance with image recording  
signals and imparted to a desired position of the  
anodic oxide layer thus dehydrated and activated; and

20                  (c) a means for fixing a dye contained in the  
ink droplets having adhered to the anodic oxide layer  
on which the recorded image has been formed, into the  
anodic oxide layer, and removing volatile components  
25 contained in the ink droplets from the anodic oxide  
layer.

                  The apparatus of the present invention may

1 preferably further comprise a means (d) for  
transporting the recording medium under heat  
insulation. The apparatus may also preferably further  
comprise a means (e) for detecting the temperature of  
5 the recording medium, a means (f) for controlling at  
least one operation of the means (a) and (c) in  
accordance with the information on the temperature,  
obtained in the temperature detecting means (e), or a  
means (g) for controlling the transport of the  
10 recording head (b) in its primary scanning direction  
and secondary scanning direction in accordance with  
the information sent from the temperature detecting  
means (e), or may preferably further comprise all of  
these means (e), (f) and (g).

15 The present invention also provides an ink  
used for making a record on an anodic oxide layer  
formed on the surface of a plate, sheet or foil made  
of aluminum or an aluminum alloy;

the ink comprising a dye having at least one  
20 group having a high reactivity.

The present invention still also provides a  
recording medium used in a process for forming an  
image by imparting ink droplets to an anodic oxide  
layer formed on the surface of a plate, sheet or foil  
25 made of aluminum or an aluminum alloy;

the recording medium comprising an image

1     forming surface overall provided with concavities  
smaller than the ink droplets and having ridges along  
their peripheries, and an anodic oxide layer formed  
thereon.

5             The present invention further provides a  
recording medium used in a process for forming an  
image by imparting ink droplets to an anodic oxide  
layer formed on the surface of a plate, sheet or foil  
made of aluminum or an aluminum alloy;

10            the recording medium being stored by a storage  
means for keeping the image forming surface away from  
the atmosphere until the image is formed by the  
method.

              The present invention still further provides a  
15     decorative aluminum plate, sheet or foil comprising a  
plate, sheet or foil made of aluminum or an alloy  
thereof and an anodic oxide layer formed on its  
surface and on which an image has been formed by  
imparting ink droplets;

20            the aluminum plate, sheet or foil being  
provided on its surface with concavities smaller than  
the ink droplets and having ridges along their  
peripheries.

              The present invention still further provides  
25     an image forming process for producing a decorative  
aluminum plate, sheet or foil, which utilizes an ink-

1 jet recording process for forming a recorded image by  
imparting ink droplets of at least one color from a  
recording head having a plurality of ink ejection  
orifices to an anodic oxide layer formed on the  
5 surface of a plate, sheet or foil made of aluminum or  
an aluminum alloy; the process comprising;

a first step of dehydrating and activating the  
anodic oxide layer;

a second step for the formation of a recorded  
10 image by causing the ink droplets to fly from the  
ejection orifices in accordance with image recording  
signals to a desired position of the anodic oxide  
layer thus dehydrated and activated, and recording a  
dot-interval image plural times by scanning the  
15 recording head plural times; and

a third step of fixing a dye contained in the  
ink droplets having adhered to the anodic oxide layer  
on which the recorded image has been formed, into the  
anodic oxide layer, and removing volatile components  
20 contained in the ink droplets from the anodic oxide  
layer.

The present invention still further provides  
an image forming process for producing a decorative  
aluminum plate, sheet or foil, which utilizes an ink-  
25 jet recording process comprising a first step of  
forming a recorded image by imparting ink droplets of

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.

Fig. 10 illustrates a specific example of the  
15        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

according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The recording medium according to 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 provided on a  
10 base comprised of a material other than aluminum or an  
alloy thereof, including various materials (substrate  
materials) as exemplified by a clad material.

Regarding the aluminum or an alloy thereof used in  
the present invention, there are no particular  
15 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 (Japan  
Industrial Standard) - 1050 and sheet or foil materials  
20 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  $\mu\text{m}$  under  
25 recording conditions of 360 dpi, and hence any surface  
treatment method that can make a concavity having a

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1 diameter of smaller than 100  $\mu\text{m}$  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  $\mu\text{m}$ .

          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/m<sup>2</sup> 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  
20 make a record. If, however, the anodic oxide layer is  
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  
25 storage shown in Fig. 5 is a manner in which the  
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 36 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.

Stated specifically, for example, dry air  
10 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  $20\text{ cm} \times 5\text{ cm}$ . 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  $\mu\text{m}$  and the  
recording is carried out under conditions of 400 dpi,  
10 it follows that one picture element has a side of  
about 63  $\mu\text{m}$  and hence about 2,400,000 cells are  
present in it, having pores with an internal volume of  
about  $0.0008 \mu\text{m}^3$  per pore. Thus, the total volume of  
the pores per picture element comes to be about 1,900  
15  $\mu\text{m}^3$ . 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  $\mu\text{m}$ . 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  $\mu\text{m}$  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  $\mu\text{m}$   
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.

5             In setting conditions as described above, when  
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  $\mu\text{m}$ , 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  $\mu\text{m}$ , 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  $1.0 \times 10^{-5}$  g/mm<sup>2</sup>·sec  
to  $1.0 \times 10^{-7}$  g/mm<sup>2</sup>·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.

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

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  
25 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  $\text{Cu}^{++}$ ,  $\text{Ni}^{++}$   
20 and  $\text{Al}^{+++}$ . 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  $\text{Cl}^-$ ,  $\text{ClCO}_3^-$  and  $\text{CH}_3\text{COO}^-$ . 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.

5             The polyvalent metal cations in the solution  
react with the reactive groups of the dye, e.g.,  
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:

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

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

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

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

1

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

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

$$h = V_d / S_d.$$

10 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  $t$  ( $\mu m$ ) is:

$$t = X V_d / S_d \quad (\mu m).$$

15 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.

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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  
20 upper half of the recording head. Record is carried  
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  $\mu\text{m}$  under recording  
            conditions of 360 dpi. Since the distance between the  
            centers of ink droplets comes to be 70.5  $\mu\text{m}$ , 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           $\mu\text{m}$ , 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 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 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 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 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.

In the case of monochromes, this brings about  
5 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.

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

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  
15 run-over, so that even dye-free areas 24 (Fig. 17A)  
are colored as shown in Fig. 17B.

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.

20 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).  
25 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  $\mu$ 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

15

20

25

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.

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.
- B: Bleeding occurs in areas where at least two
- 15 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

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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  $\mu\text{m}$  each had been  
formed and aluminum sheets (B) on which anodic oxide  
layers (aluminum anodic oxide layers) with a layer  
10 thickness of 20  $\mu\text{m}$  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  $\mu\text{m}$ , 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  $\mu\text{m}$ , a better image quality is attained when the  
glycerol is in a percentage of 10% or less.

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Table 3

1

| Amount of<br>glycerol<br>(g) | A<br>10µm thick layer | B<br>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-0-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<br>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  $\mu\text{m}$  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  $\text{AlCl}_3$   
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<br>reflection density: | 85% or more | Less than 80% |

15

As described above, according to the image  
forming process of 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 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 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 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 EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1

1. An image forming process for the formation  
of a recorded image by imparting ink droplets of at  
least one color from a recording head having a  
5 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  
15 activated; and

a third step of fixing a dye contained in the  
ink droplets having adhered to the anodic oxide layer  
on which said recorded image has been formed, into  
said anodic oxide layer, and removing volatile  
20 components contained in said ink droplets from said  
anodic oxide layer.

2. The image forming process according to  
claim 1, wherein said ink comprises multi-color inks  
25 to form a colored recorded image.

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1           3. The image forming process according to  
claim 1 or 2, wherein each treatment applied to the  
anodic oxide layer in at least one of the first step  
and the third step is a heat treatment for the layer.

5

          4. The image forming process according to  
claim 1 or 2, wherein each treatment applied to the  
anodic oxide layer in at least one of the first step  
and the third step is an electromagnetic induction  
10 treatment.

          5. The image forming process according to  
claim 1 or 2, wherein each treatment applied to the  
anodic oxide layer in at least one of the first step  
15 and the third step is a dry-air blowing treatment.

          6. The image forming process according to  
claim 1 or 2, wherein the third step comprises a  
treatment of rinsing the layer with water.

20

          7. The image forming process according to  
claim 1, wherein the step of forming an image by  
causing the ink droplets to fly is carried out by  
bubble-jet recording.

25

          8. A process for producing a decorative

1 aluminum plate, sheet or foil, comprising forming a  
recorded image by imparting ink droplets of at least  
one color from a recording head having a plurality of  
ink ejection orifices to an anodic oxide layer formed  
5 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;  
a second step for the formation of a recorded  
10 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  
15 a third step of fixing a dye contained in the  
ink droplets having adhered to the 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  
20 anodic oxide layer.

9. The process for producing a decorative  
aluminum plate, sheet or foil according to claim 8,  
wherein said ink comprises multi-color inks to form a  
25 colored recorded image.

1           10. The process for producing a decorative  
aluminum plate, sheet or foil according to claim 8 or  
9, wherein each treatment applied to the anodic oxide  
layer in at least one of the first step and the third  
5 step is a heat treatment for the layer.

11. The process for producing a decorative  
aluminum plate, sheet or foil according to claim 8 or  
9, wherein each treatment applied to the anodic oxide  
10 layer in at least one of the first step and the third  
step is an electromagnetic induction treatment.

12. The process for producing a decorative  
aluminum plate, sheet or foil according to claim 8 or  
15 9, wherein each treatment applied to the anodic oxide  
layer in at least one of the first step and the third  
step is a dry-air blowing treatment.

13. The process for producing a decorative  
20 aluminum plate, sheet or foil according to claim 8 or  
9, wherein the third step comprises a treatment of  
rinsing the layer with water.

14. The process for producing a decorative  
25 aluminum plate, sheet or foil according to claim 8,  
wherein the step of forming an image by causing the

1     ink droplets to fly is carried out by bubble-jet  
recording.

15           15.    An apparatus for producing a decorative  
aluminum plate, sheet or foil by forming a recorded  
image on a recording medium having an anodic oxide  
layer formed on the surface of a plate, sheet or foil  
made of aluminum or an aluminum alloy, by imparting  
ink droplets of at least one color to said anodic  
10   oxide layer formed thereon, comprising;

          (a) a means for dehydrating and activating  
said anodic oxide layer;

          (b) a recording head having a plurality of ink  
ejection orifices from which the ink droplets are  
15   caused to fly in accordance with image recording  
signals and imparted to a desired position of the  
anodic oxide layer thus dehydrated and activated; and

          (c) a means for fixing a dye contained in the  
ink droplets having adhered to the anodic oxide layer  
20   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.

25           16.    The apparatus according to claim 15,  
which further comprises a means (d) for transporting

1     said recording medium under heat insulation.

17.   The apparatus according to claim 15 or  
16, which further comprises at least one of;

5             (e) a means for detecting the temperature of  
said recording medium; and

             (f) a means for controlling at least one  
operation of the means (a) and (c) in accordance with  
the information on the temperature, obtained in the  
10    temperature detecting means (e).

18.   The apparatus according to claim 15,  
wherein said recording head (b) scans over said anodic  
oxide layer to record the image; and said apparatus  
15    further comprising;

             (e) a means for detecting the temperature of  
said recording medium; and

             (g) a means for controlling the transport of  
the recording head (b) in its primary scanning  
20    direction and secondary scanning direction in  
accordance with the information sent from the  
temperature detecting means (e).

19. A decorative aluminum plate, sheet or foil comprising a plate, sheet or foil made of aluminum or an alloy thereof and an anodic oxide layer formed on its surface and on which an image has been formed by imparting ink droplets;

said aluminum plate, sheet or foil being provided on its surface with concavities smaller than the ink droplets and having ridges along their peripheries.

20. An image forming process for the formation of a recorded image using an ink-jet recording process by imparting ink droplets of 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, comprising:

a first step of dehydrating and activating said anodic oxide layer;

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 to a desired position of the anodic oxide layer thus dehydrated and activated, and recording a dot-interval image plural times by scanning of the recording head plural times; and

a third step of fixing a dye contained in the ink droplets having adhered to the anodic oxide layer on which the recorded image has been formed, into the anodic oxide layer, and removing volatile components contained in the ink droplets from said anodic oxide layer.

21. The image recording process according to claim 20, wherein in the second step said dot-interval image is recorded in such a manner that the dots recorded by each scanning of the recording head do not become continuous on the anodic oxide layer.

22. The image recording process according to claim 20, wherein in the second step, in the case when next ink droplets are imparted adjacently to ink droplets first imparted, the next ink droplets are imparted after volatile components in the first ink droplets have evaporated.

23. The image recording process according to claim 20, wherein in the second step, in the case when next ink droplets are imparted superimposingly to ink droplets first imparted, the next ink droplets are imparted after volatile components in the first ink droplets have evaporated.

24. The image forming process according to claim

20, wherein said ink comprises multi-color inks to form a colored recorded image.

25. The image forming process according to any one of claims 20 to 24, wherein each treatment applied to the anodic oxide layer in at least one of the first step and the third step is a heat treatment for the layer.

26. The image forming process according to any one of claims 20 to 24, wherein each treatment applied to the anodic oxide layer in at least one of the first step and the third step is an electromagnetic induction treatment.

27. The image forming process according to any one of claims 20 to 24, wherein each treatment applied to the anodic oxide layer in at least one of the first step and the third step is a dry-air blowing treatment.

28. The image forming process according to any one of claims 20 to 24, wherein the third step comprises a treatment of rinsing the layer with water.

29. The image forming process according to claim 20, wherein said ink-jet recording process is a bubble-jet recording process.

30. A process for producing a decorative aluminum

plate, sheet or foil using an ink-jet recording process by imparting ink droplets of 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, comprising:

a first step of dehydrating and activating said anodic oxide layer;

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 to a desired position of the anodic oxide layer thus dehydrated and activated, and recording a dot-interval image plural times by scanning of the recording head plural times; and

a third step of fixing a dye contained in the ink droplets having adhered to the anodic oxide layer on which the recorded image has been formed, into the anodic oxide layer, and removing volatile components contained in the ink droplets from said anodic oxide layer.

31. An image forming process for the formation of a recorded image using an ink-jet recording process comprising a first step of forming a recorded image by imparting ink droplets of 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 step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer on which the recorded image has been formed.

32. The image forming process according to claim 31, which further comprises, prior to the first step, the step of dehydrating and activating said anodic oxide layer.

33. The image forming process according to claim 31, wherein said ink-jet recording process is a bubble-jet recording process.

34. A process for producing a decorative aluminum plate, sheet or foil using an ink-jet recording process comprising a first step of forming a recorded image by imparting ink droplets of 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 step of applying an aqueous polyvalent metal salt solution to the anodic oxide layer on which the recorded image has been formed.

35. The process for producing a decorative aluminum

plate, sheet or foil according to claim 34, which further comprises, prior to the first step, the step of dehydrating and activating said anodic oxide layer.

36. The process for producing a decorative aluminum plate, sheet or foil according to claim 34, wherein said ink-jet recording process is a bubble-jet recording process.

FIG. 1

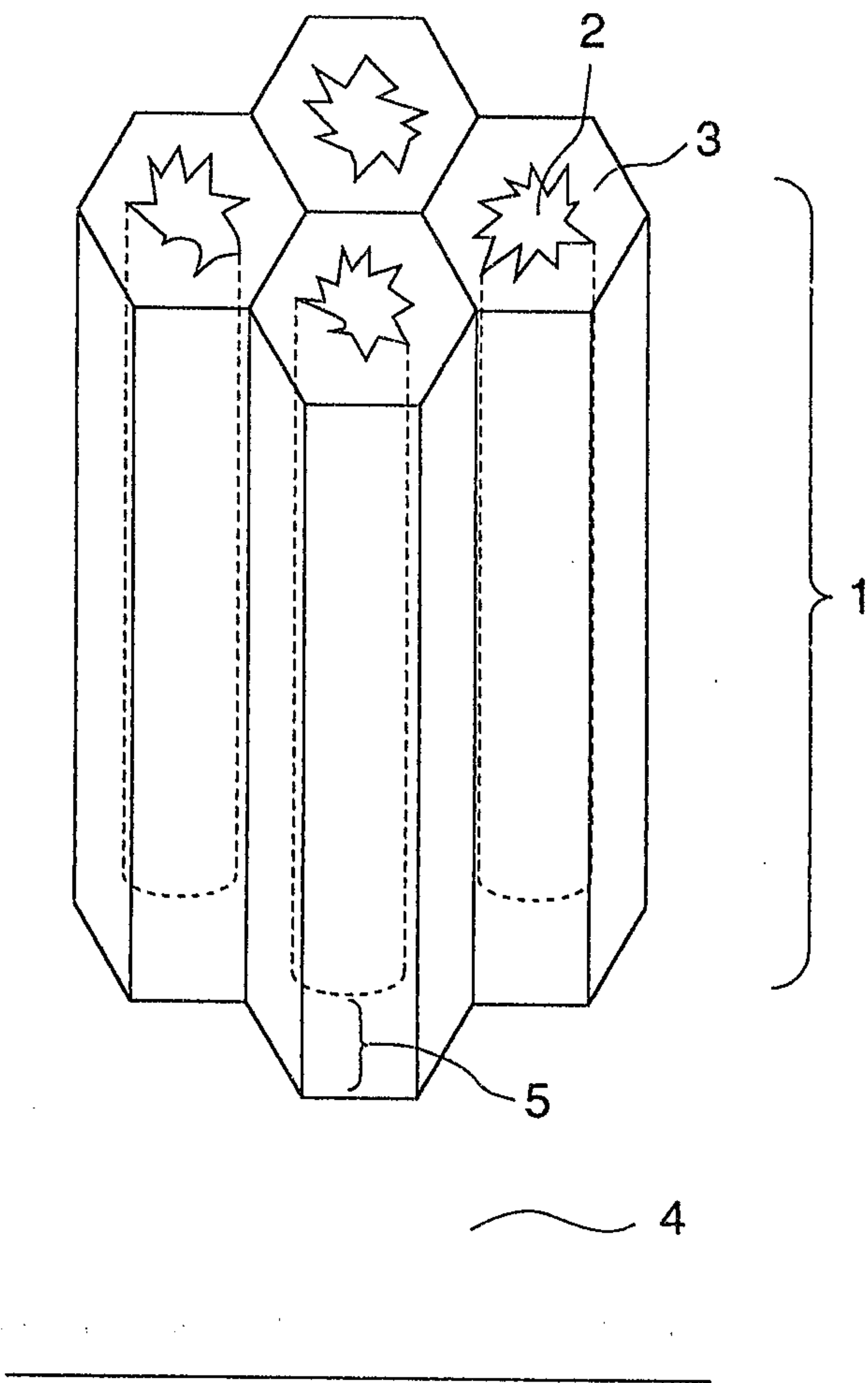


FIG. 2A

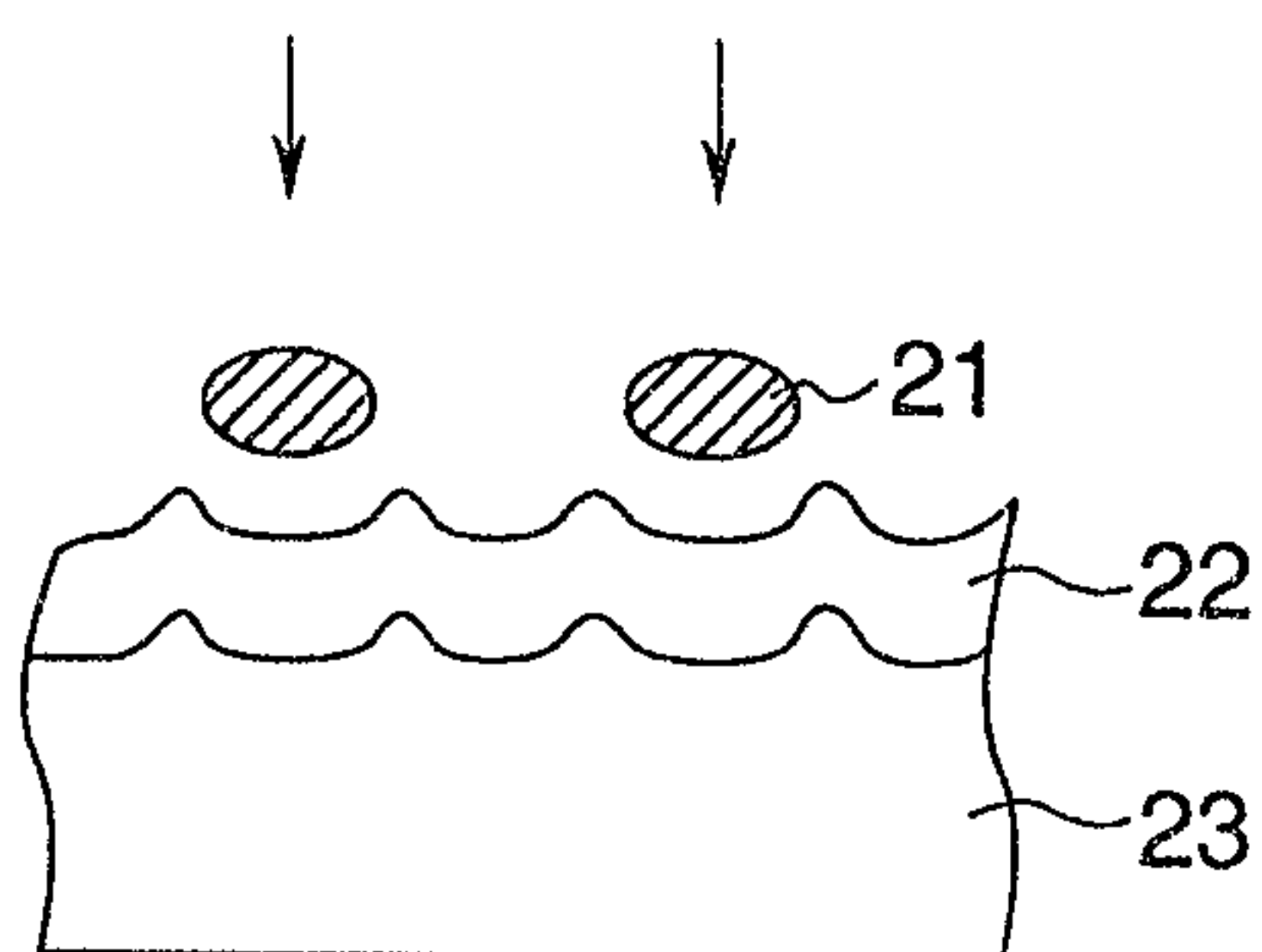


FIG. 2D

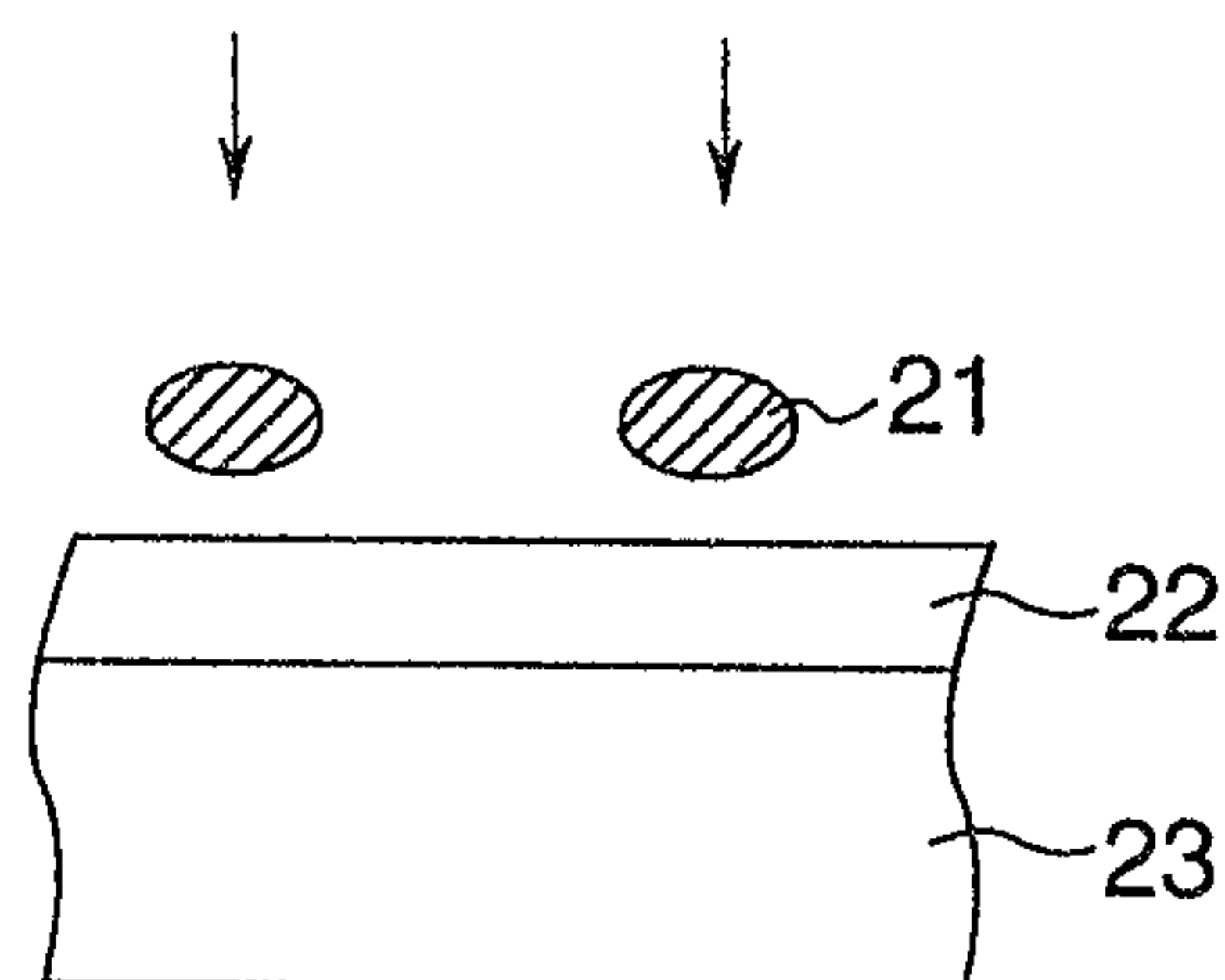


FIG. 2B

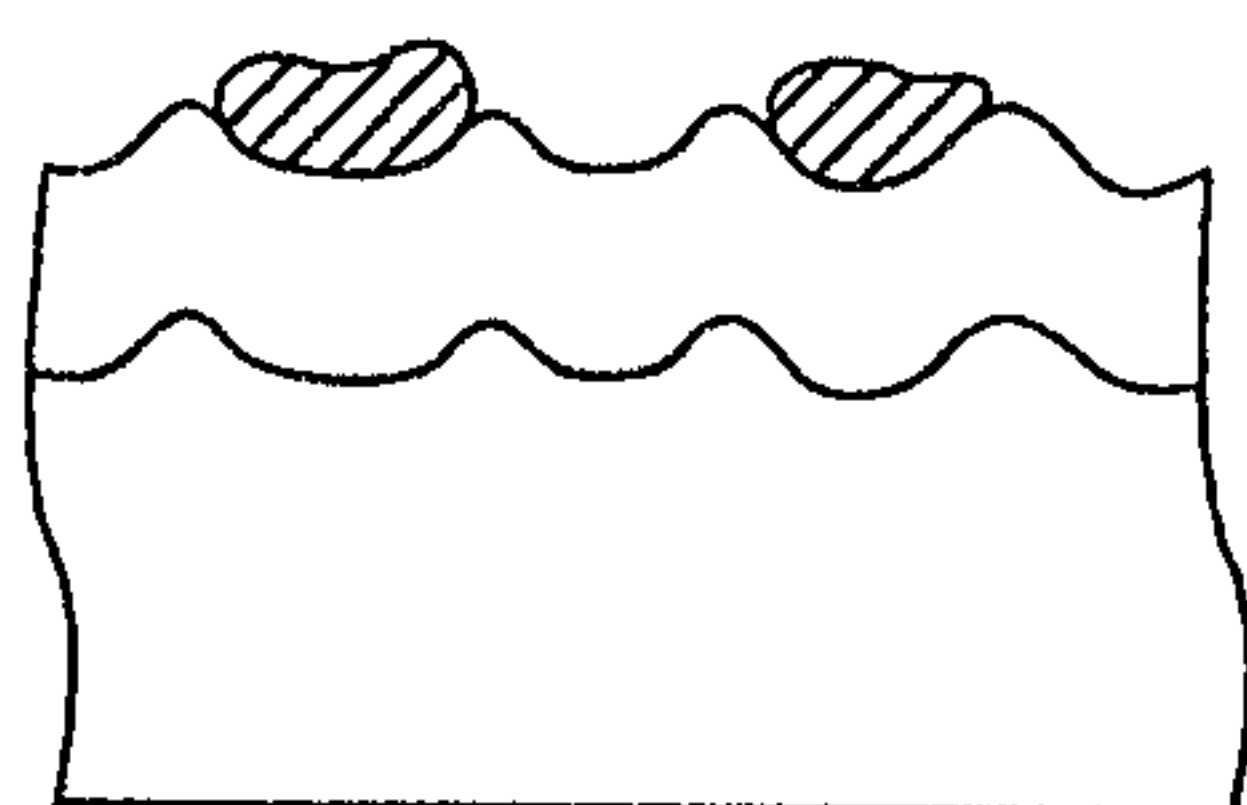


FIG. 2E

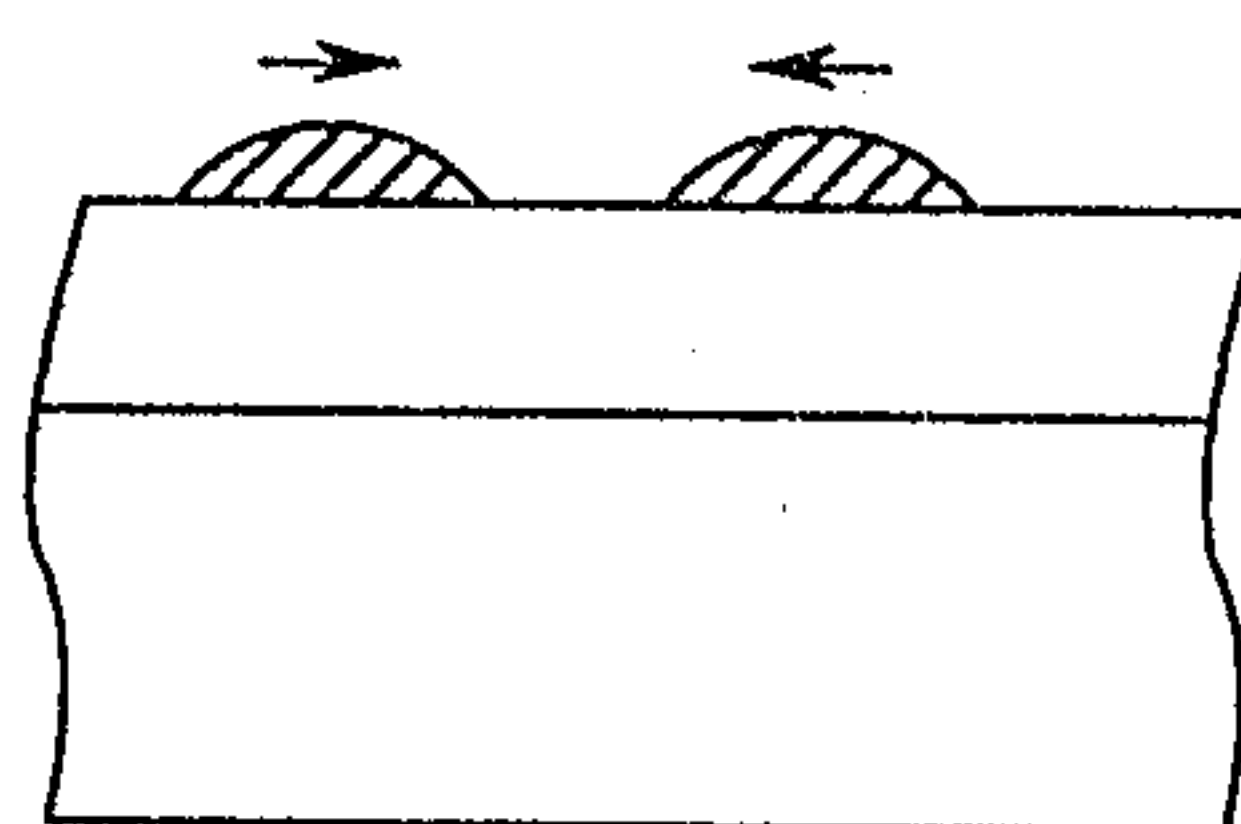


FIG. 2C

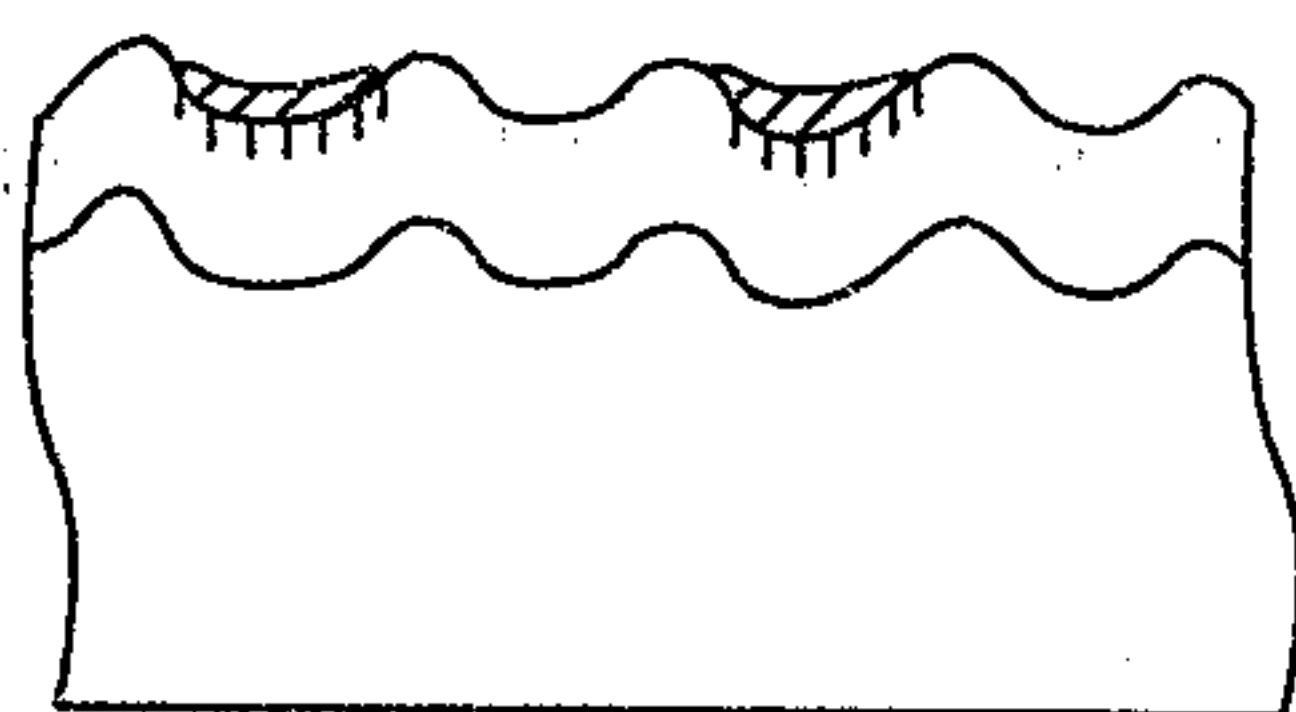


FIG. 2F

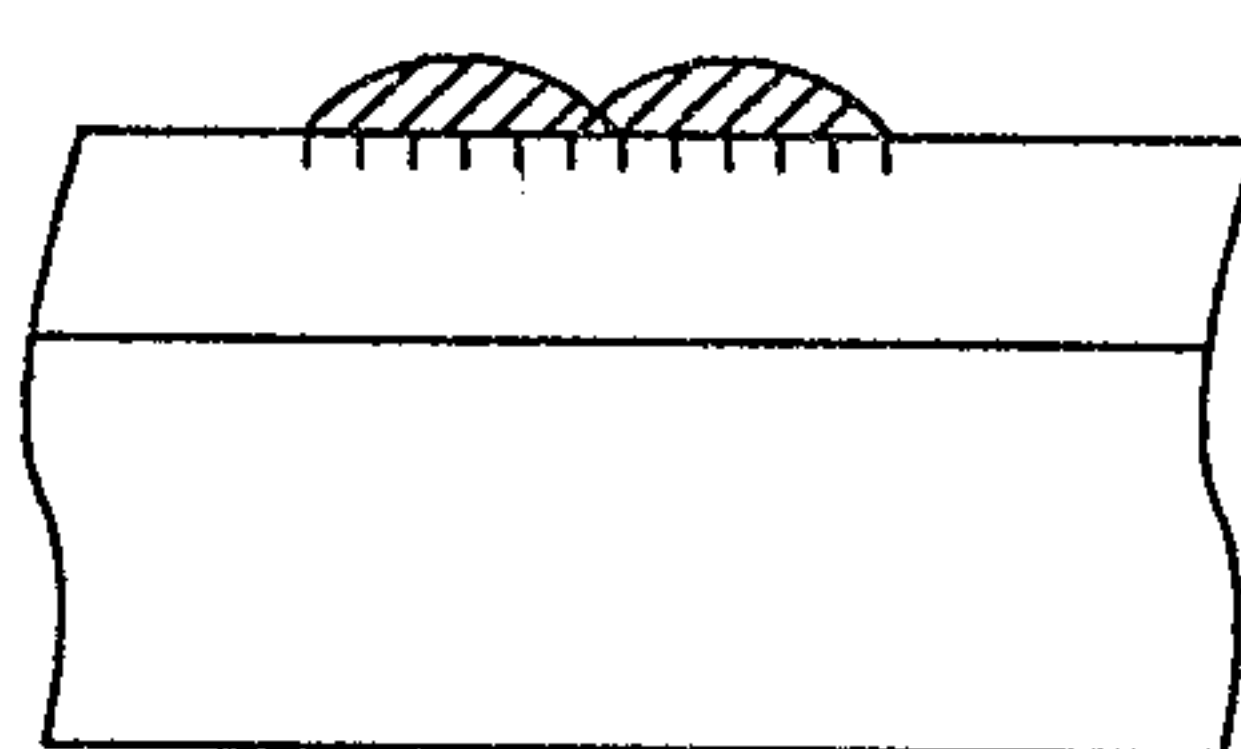


FIG. 3

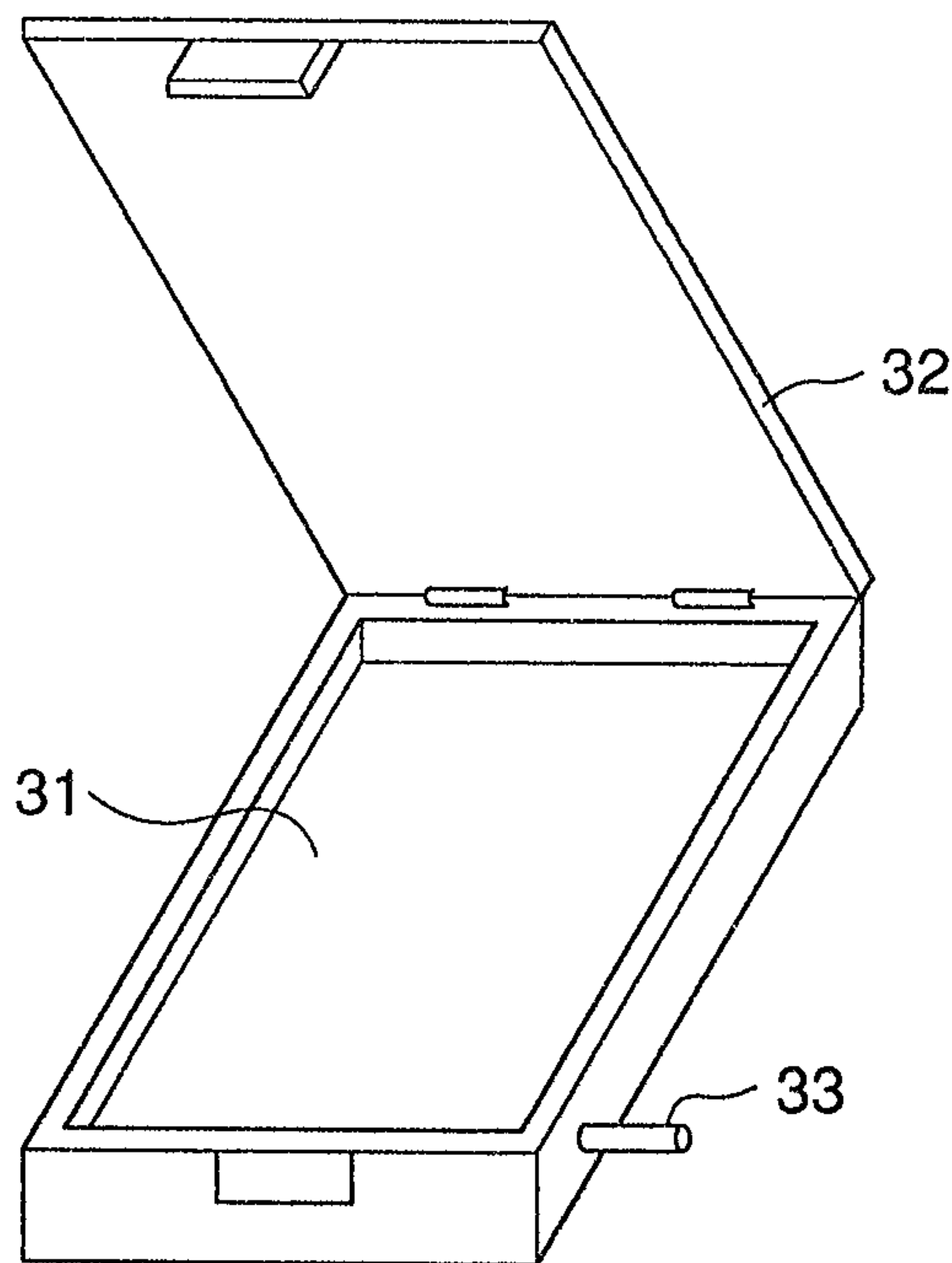
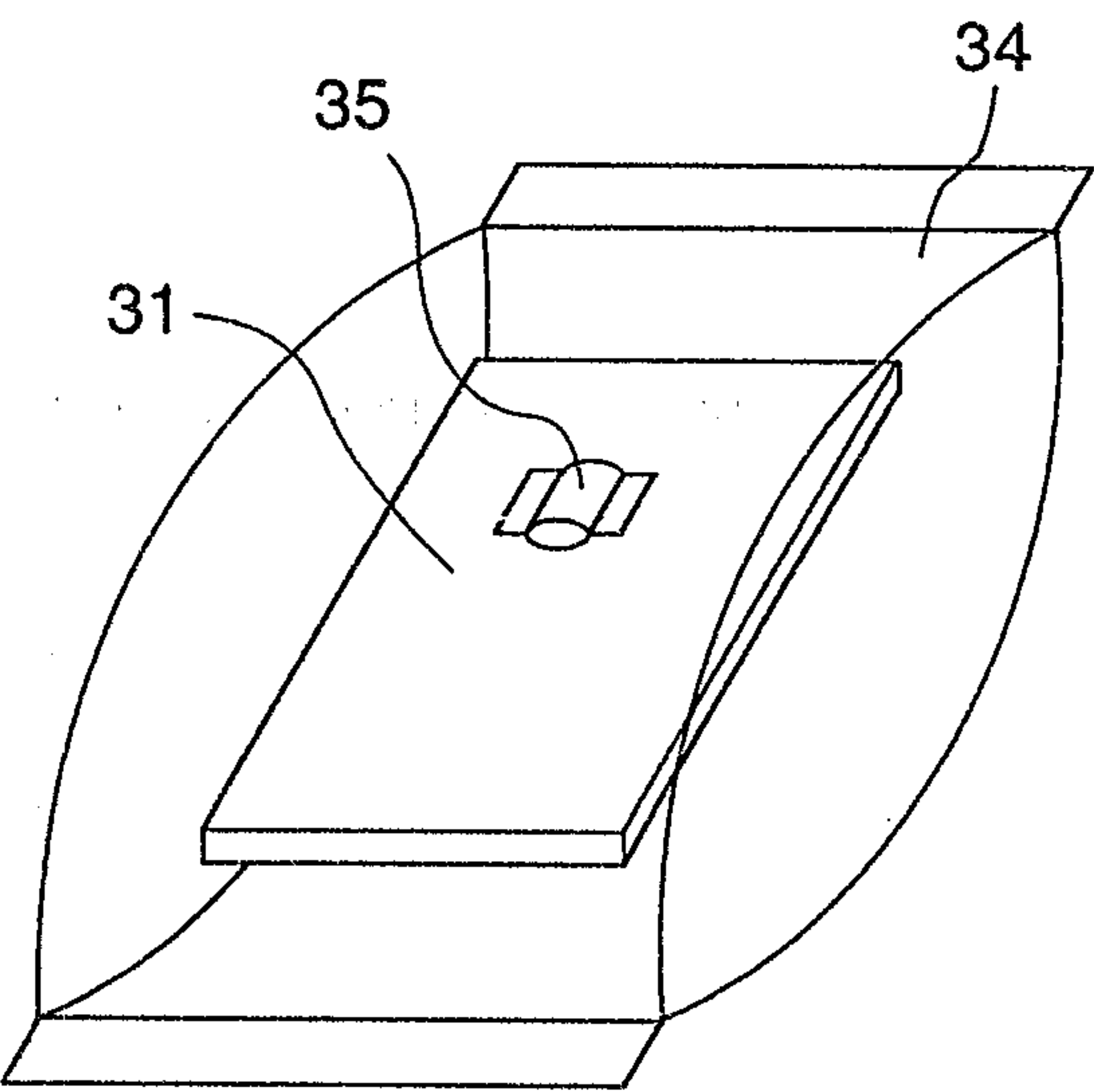


FIG. 4



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FIG. 5

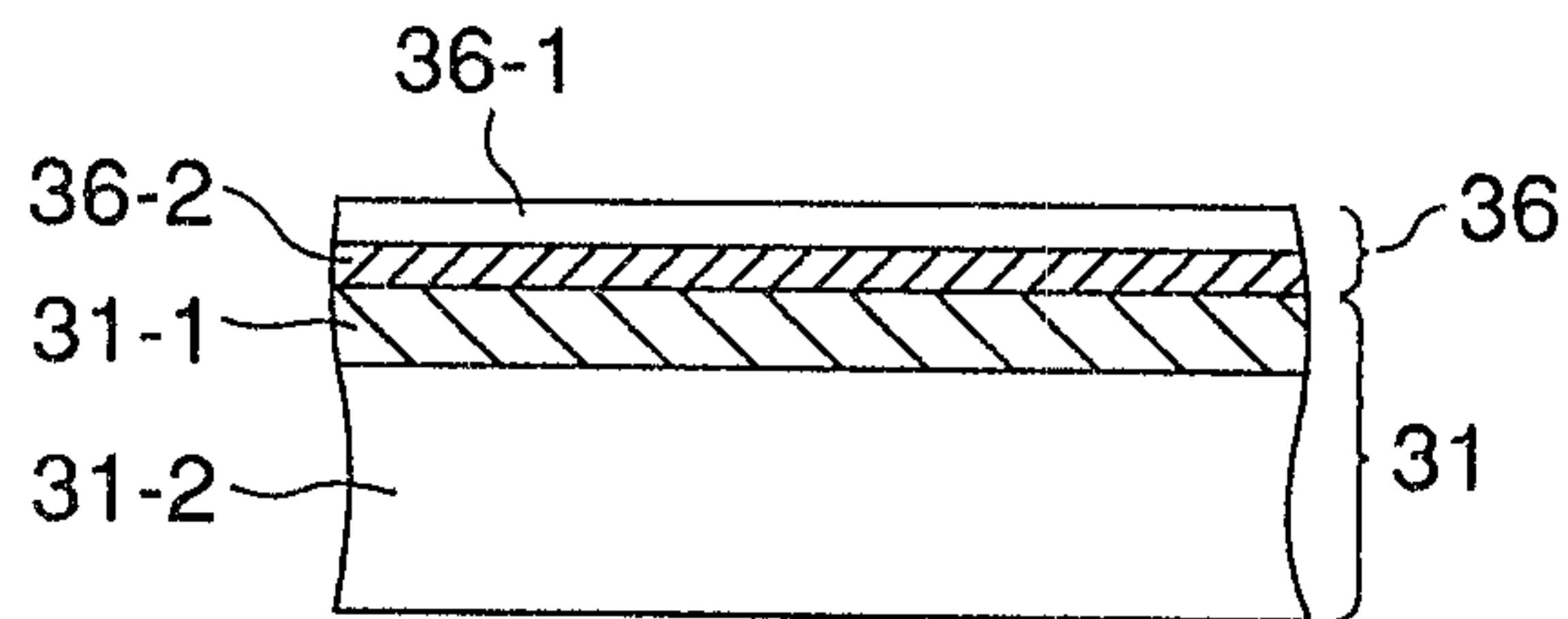
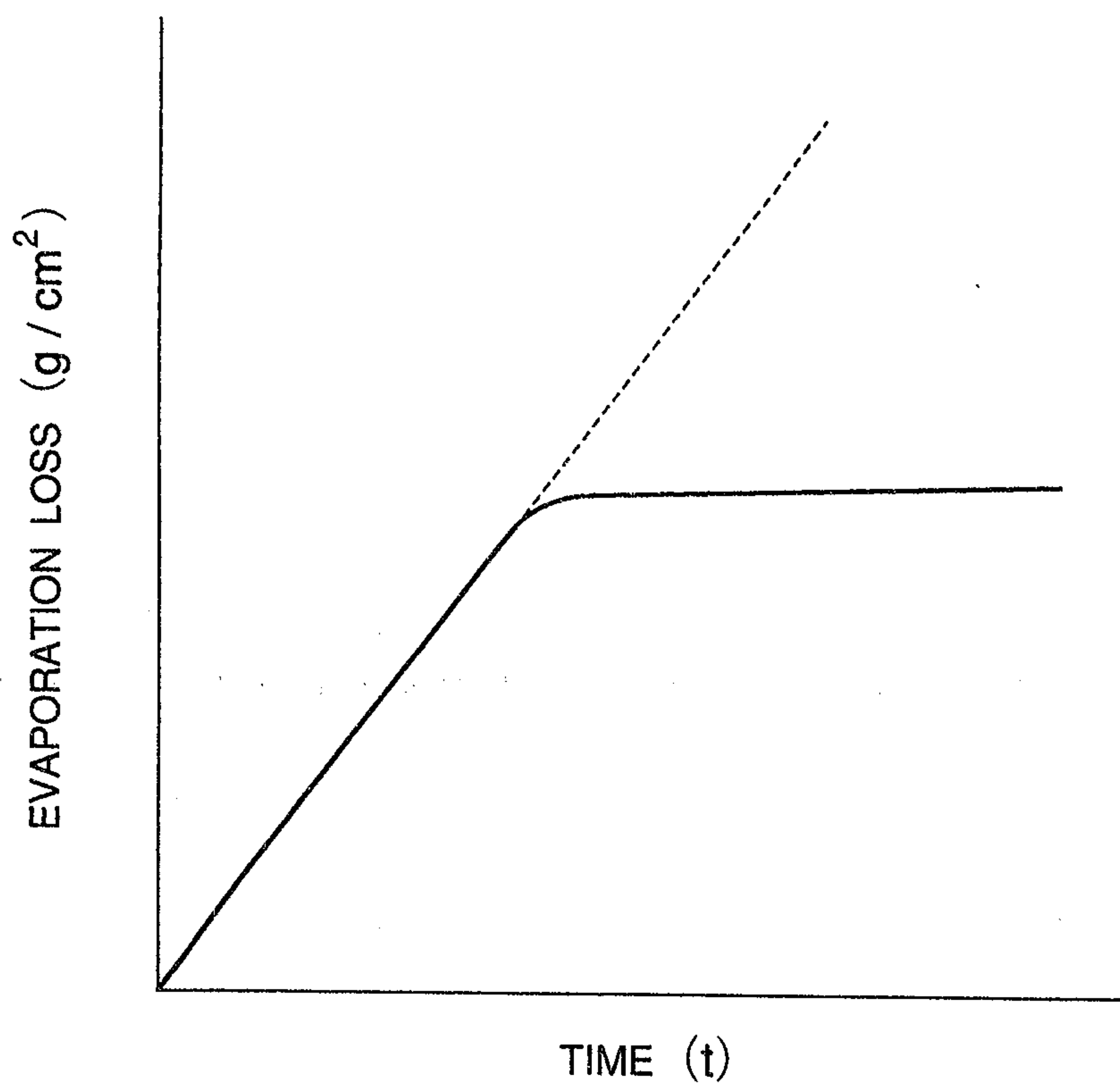


FIG. 6



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FIG. 7

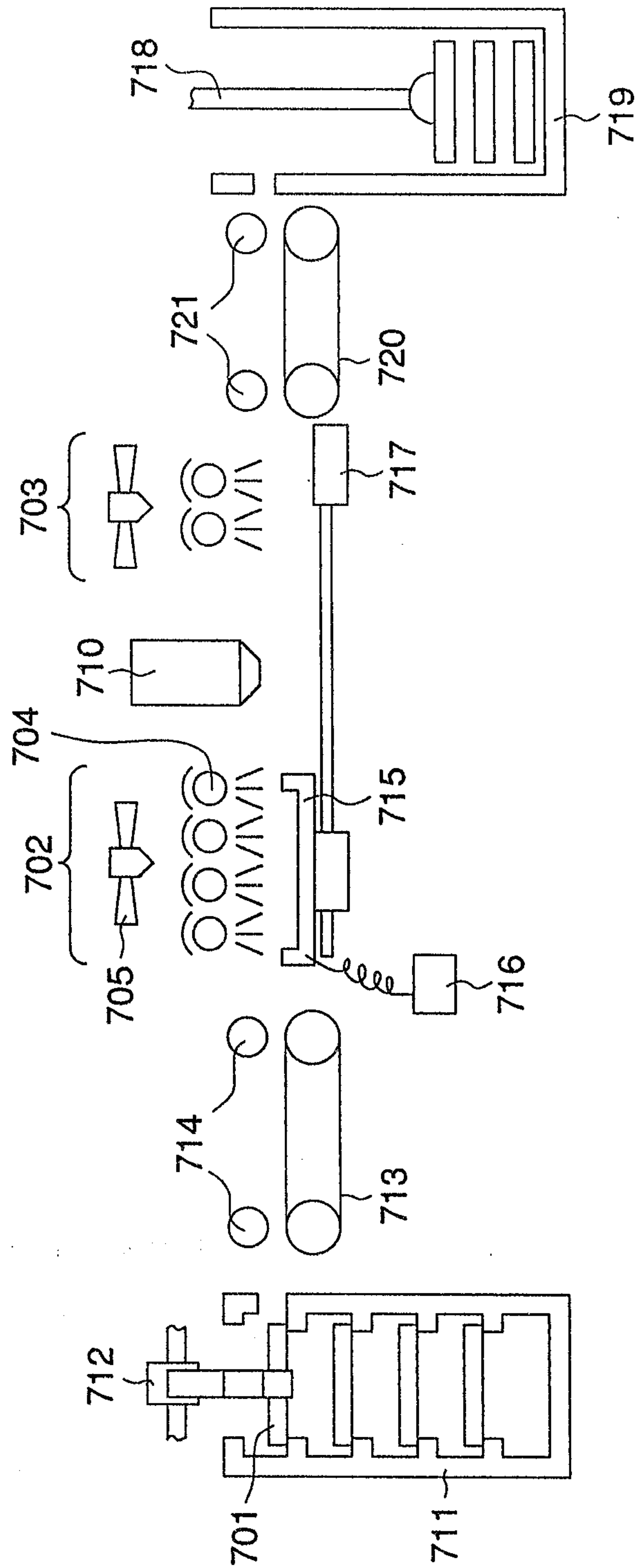


FIG. 8

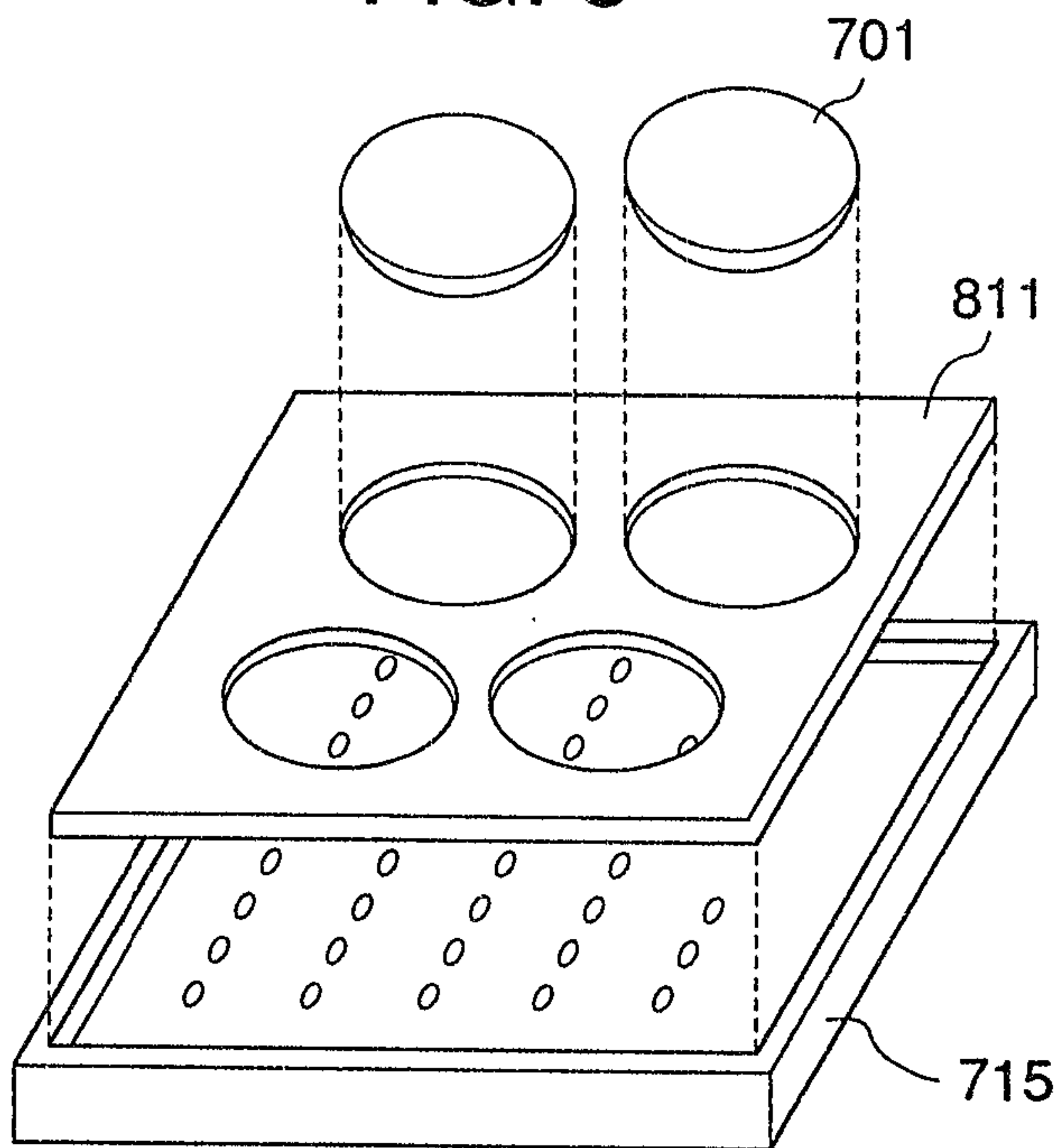


FIG. 9

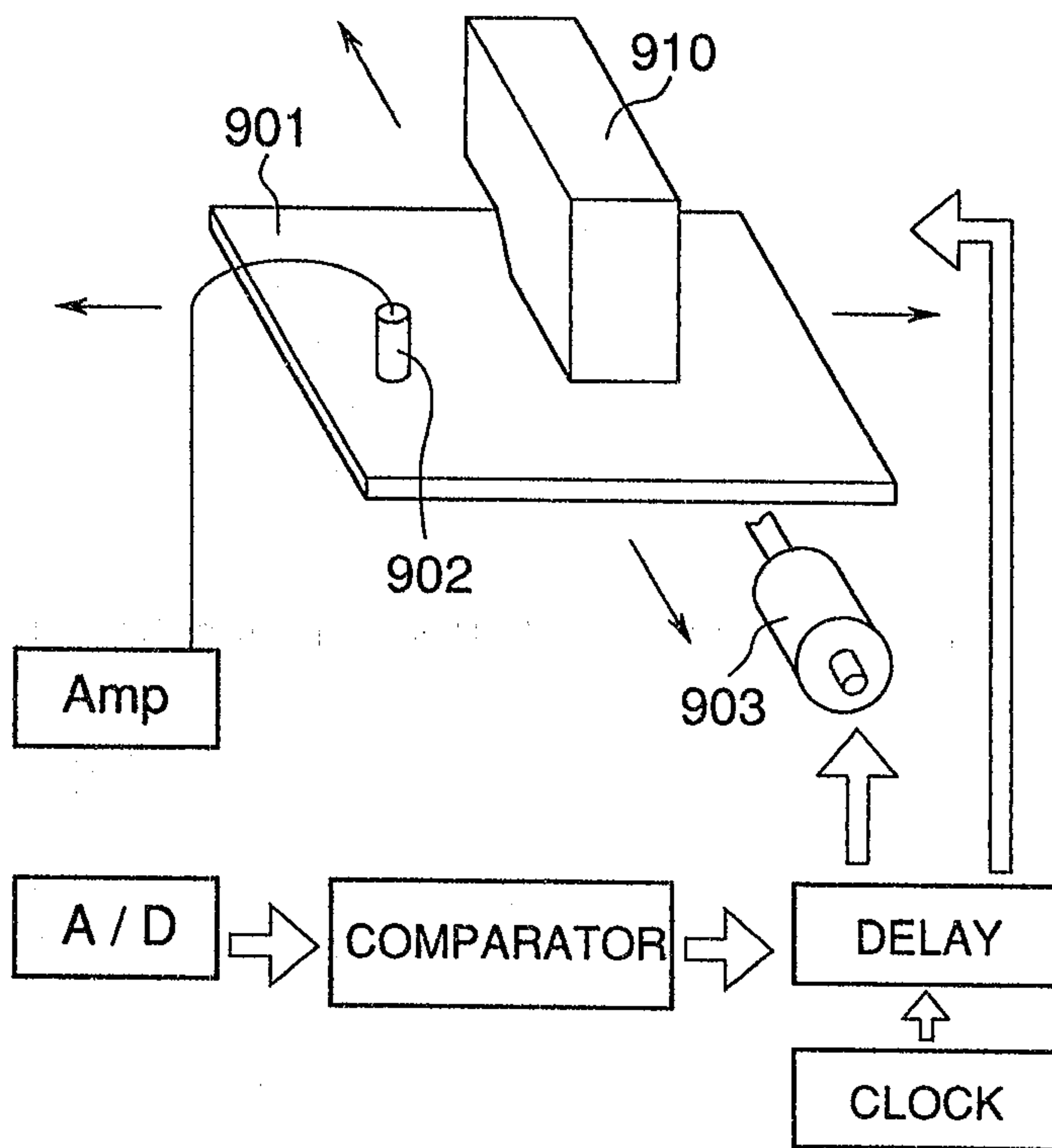


FIG. 10

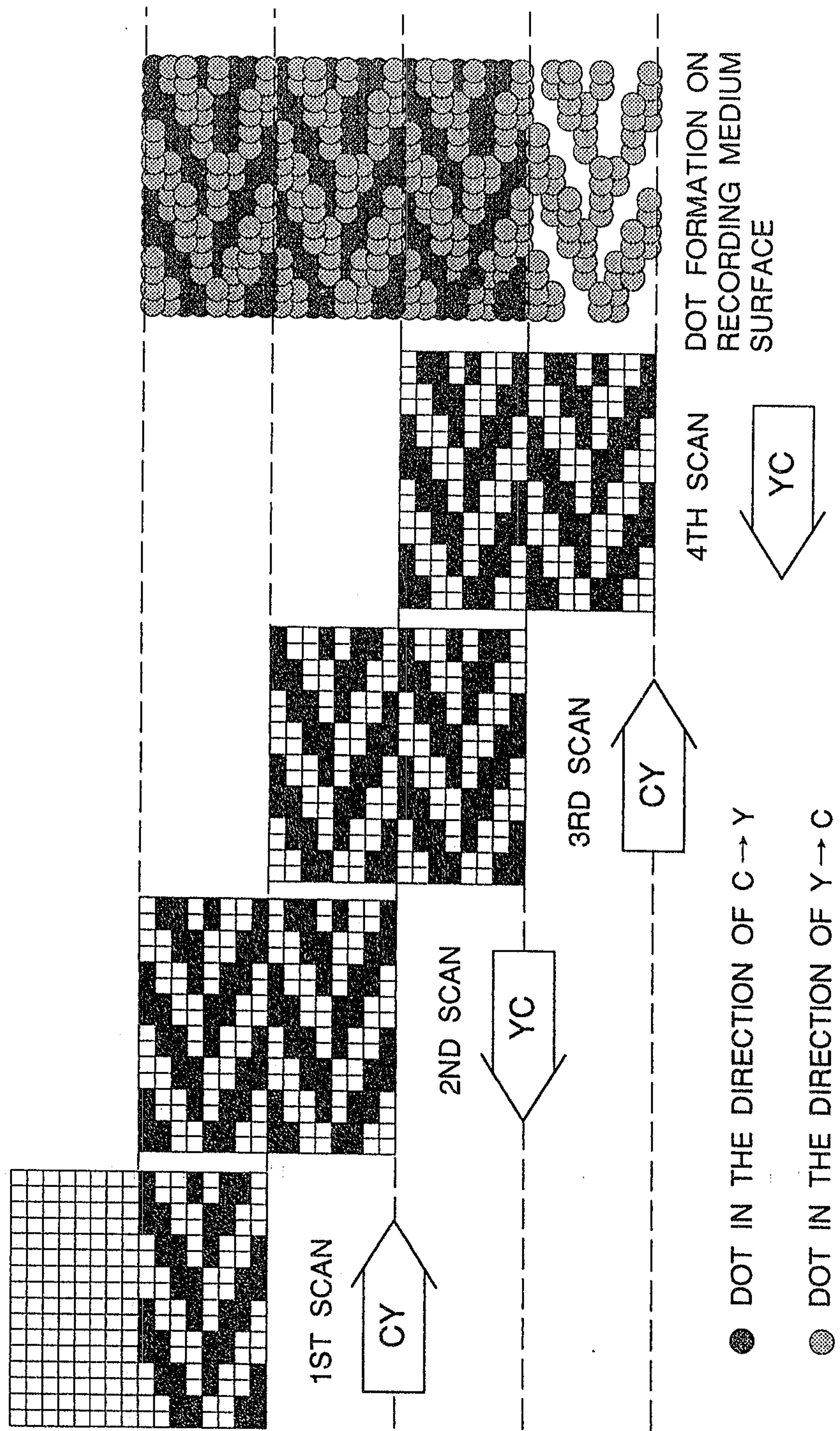
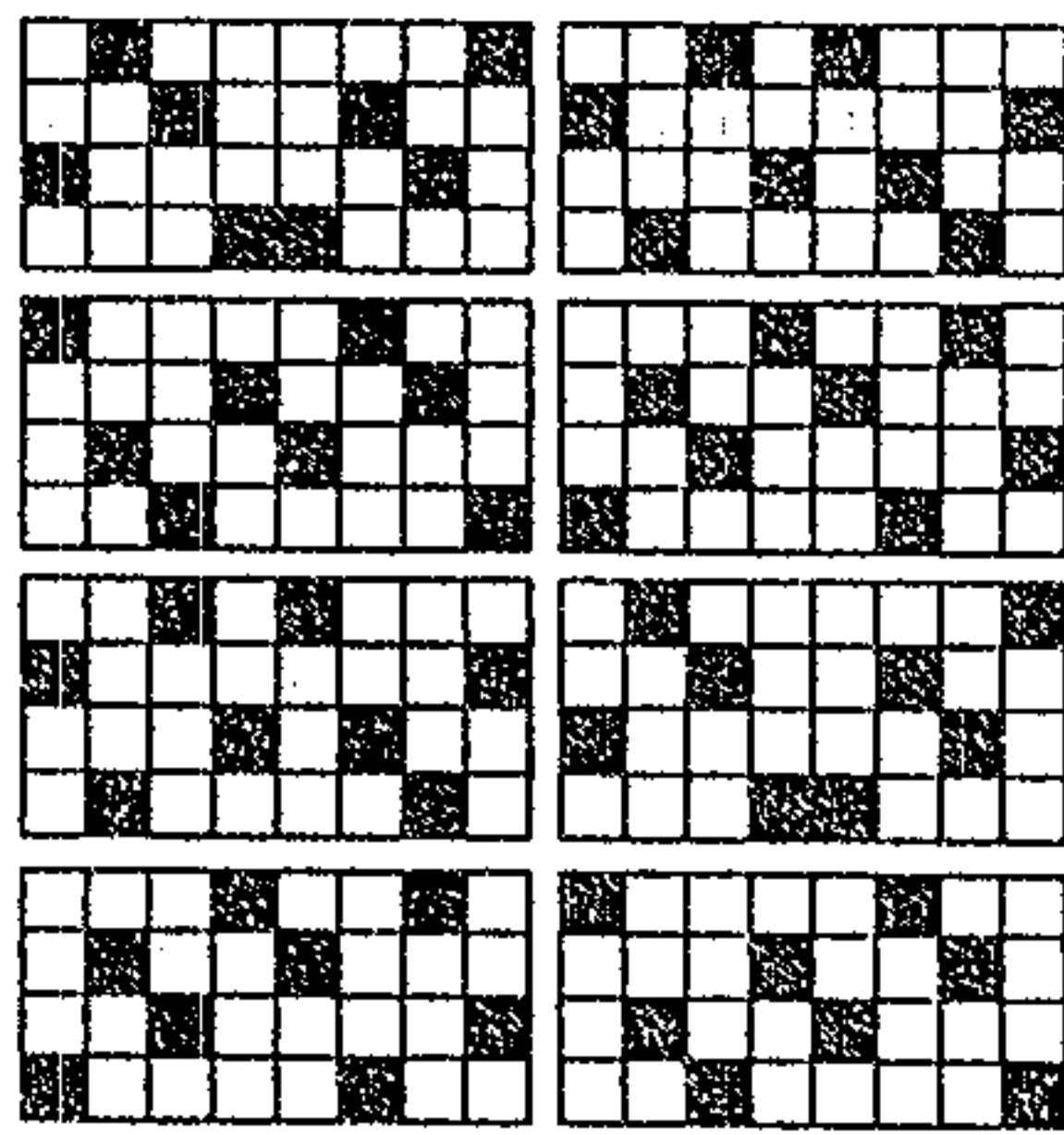


FIG. 11A

1st-pass



Bk

FIG. 11B

2nd-pass

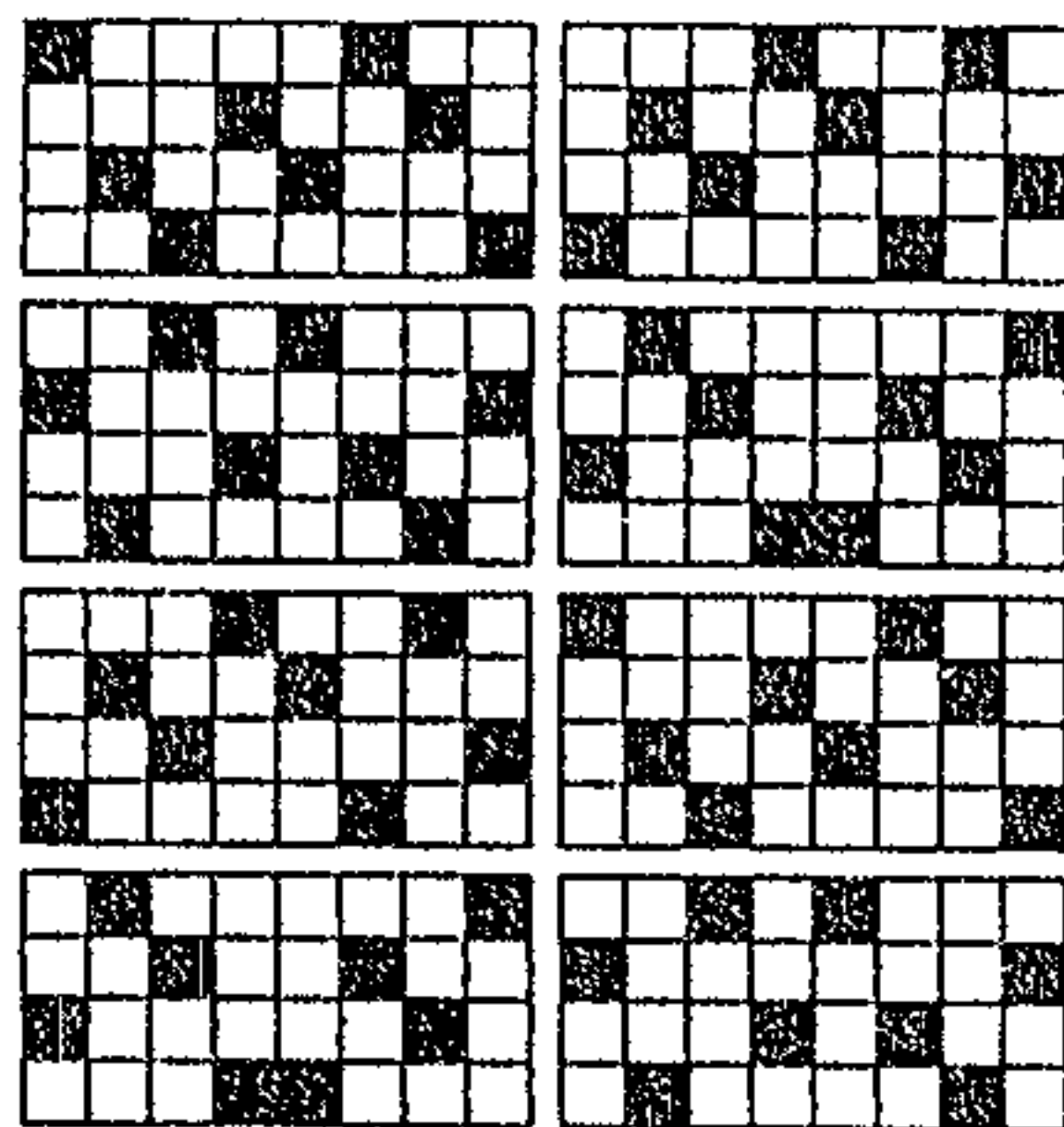


FIG. 11C

3rd-pass

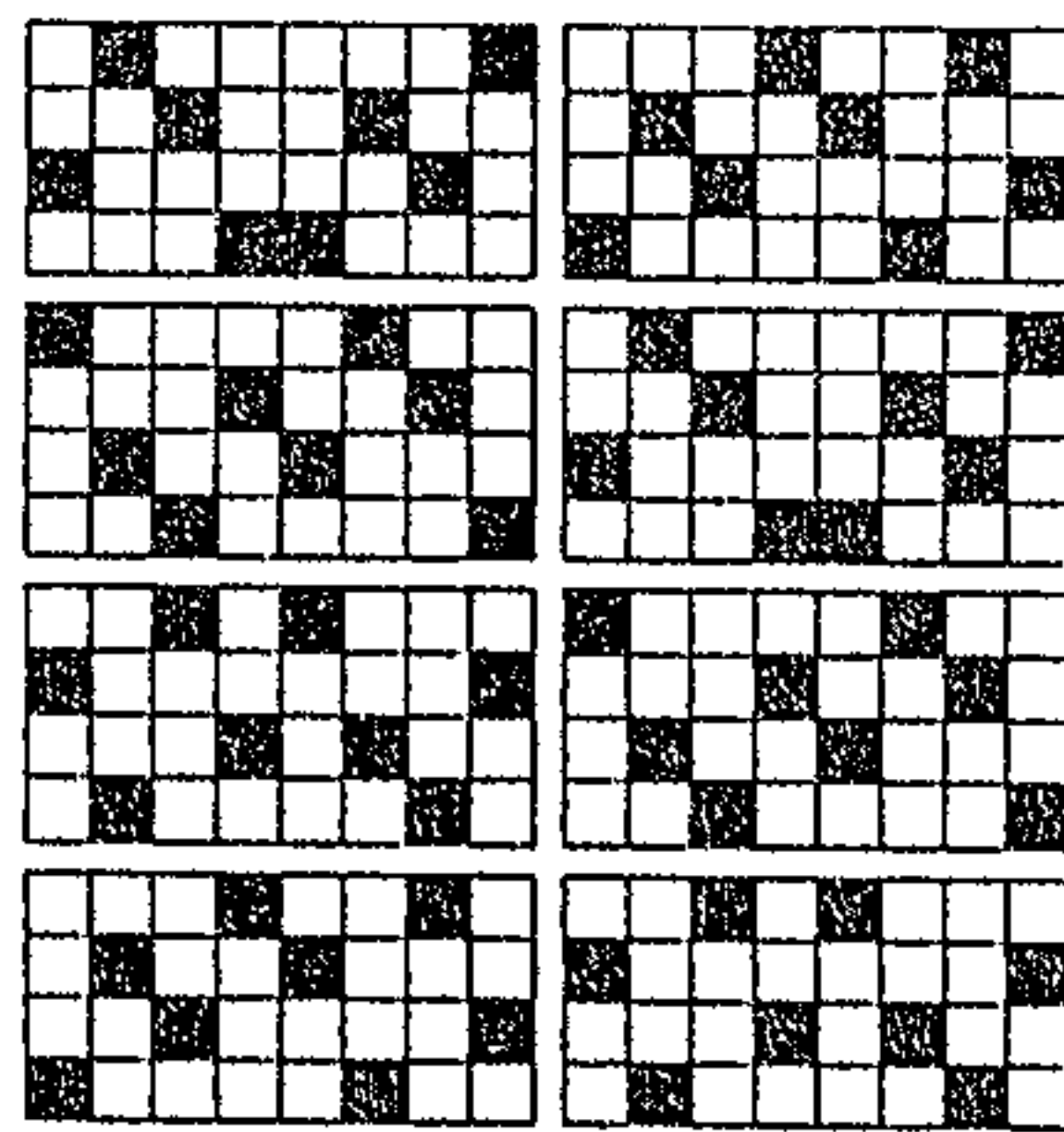


FIG. 11D

4th-pass

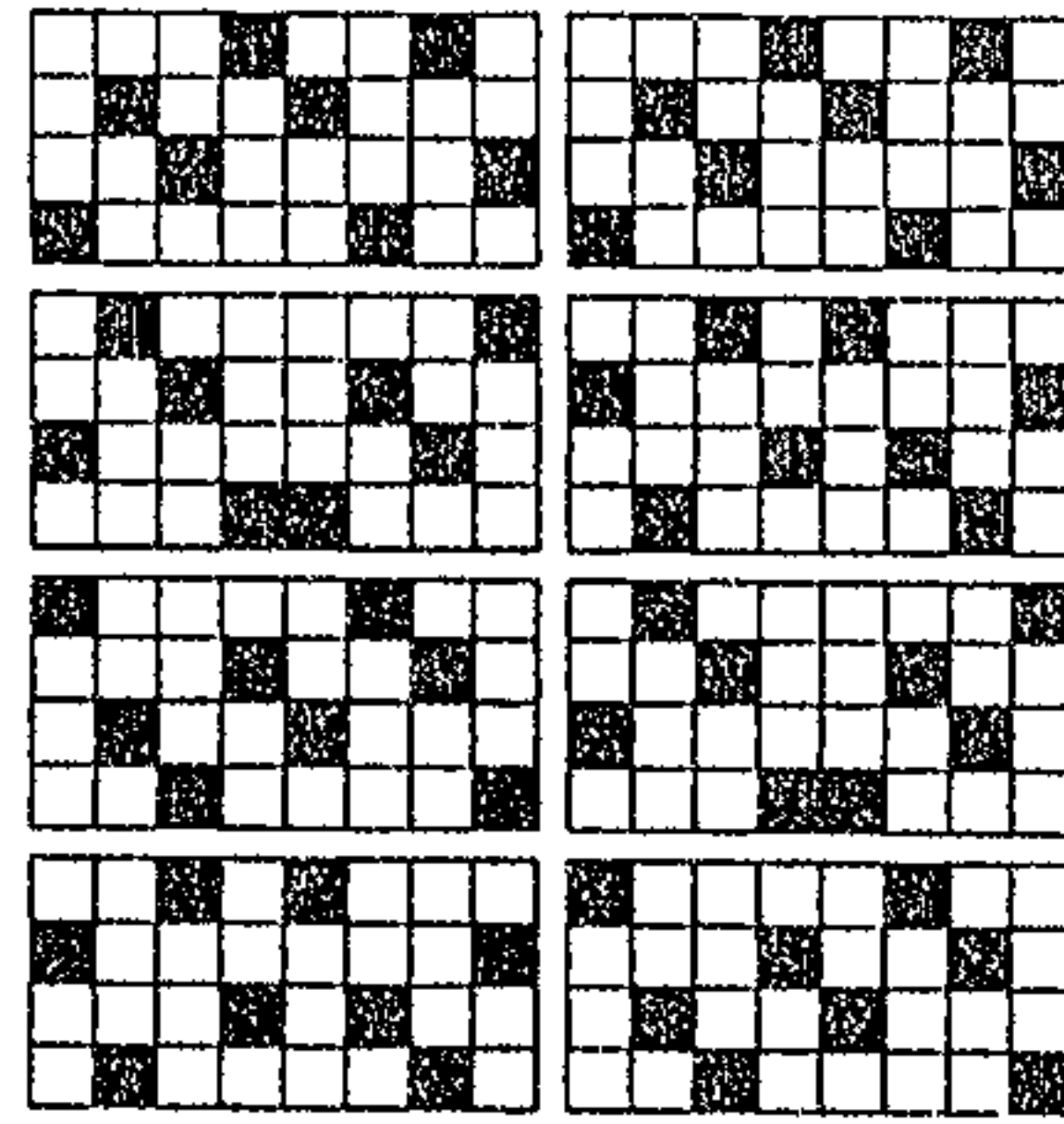
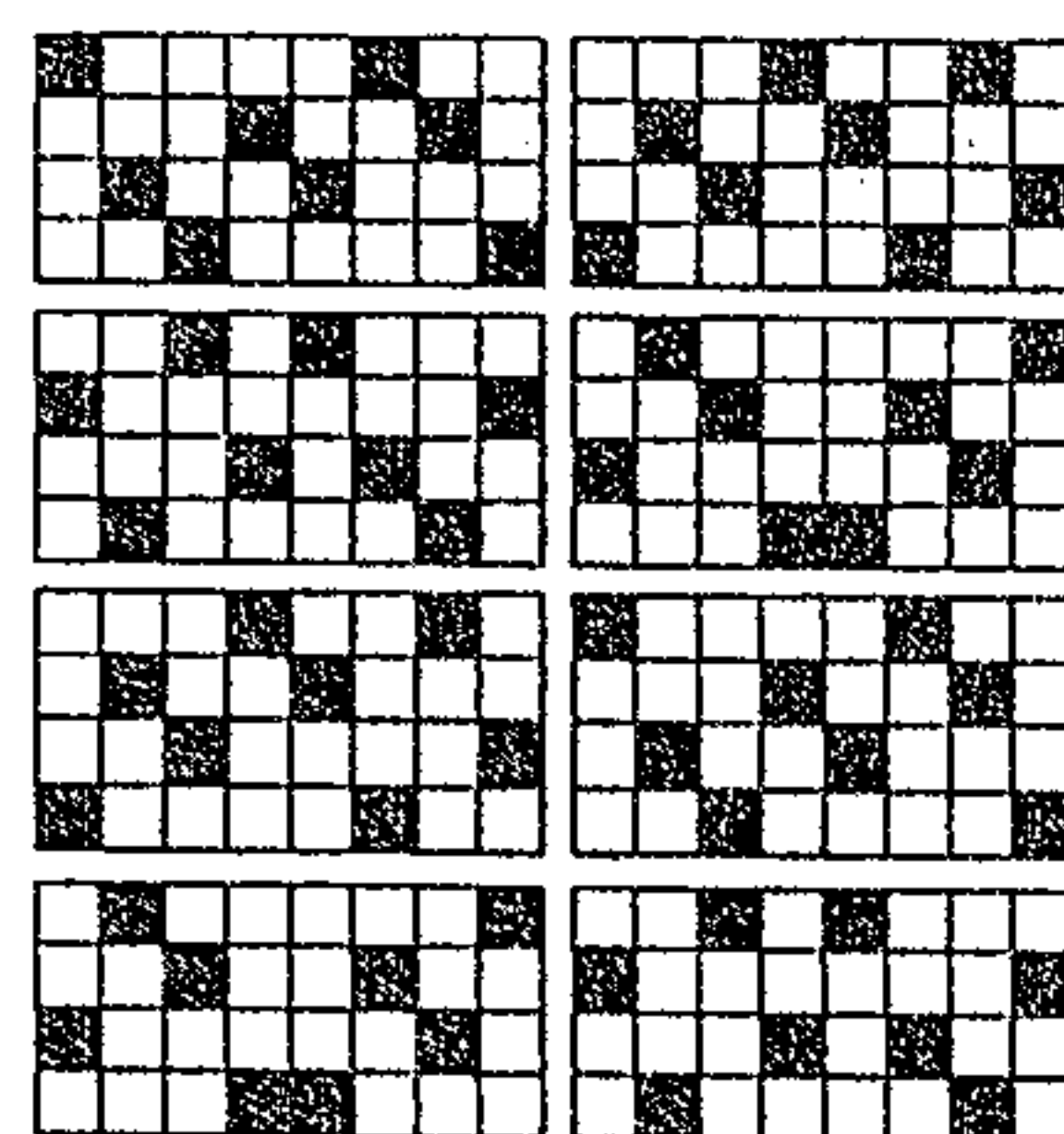


FIG. 11E

1st-pass



C

FIG. 11F

2nd-pass

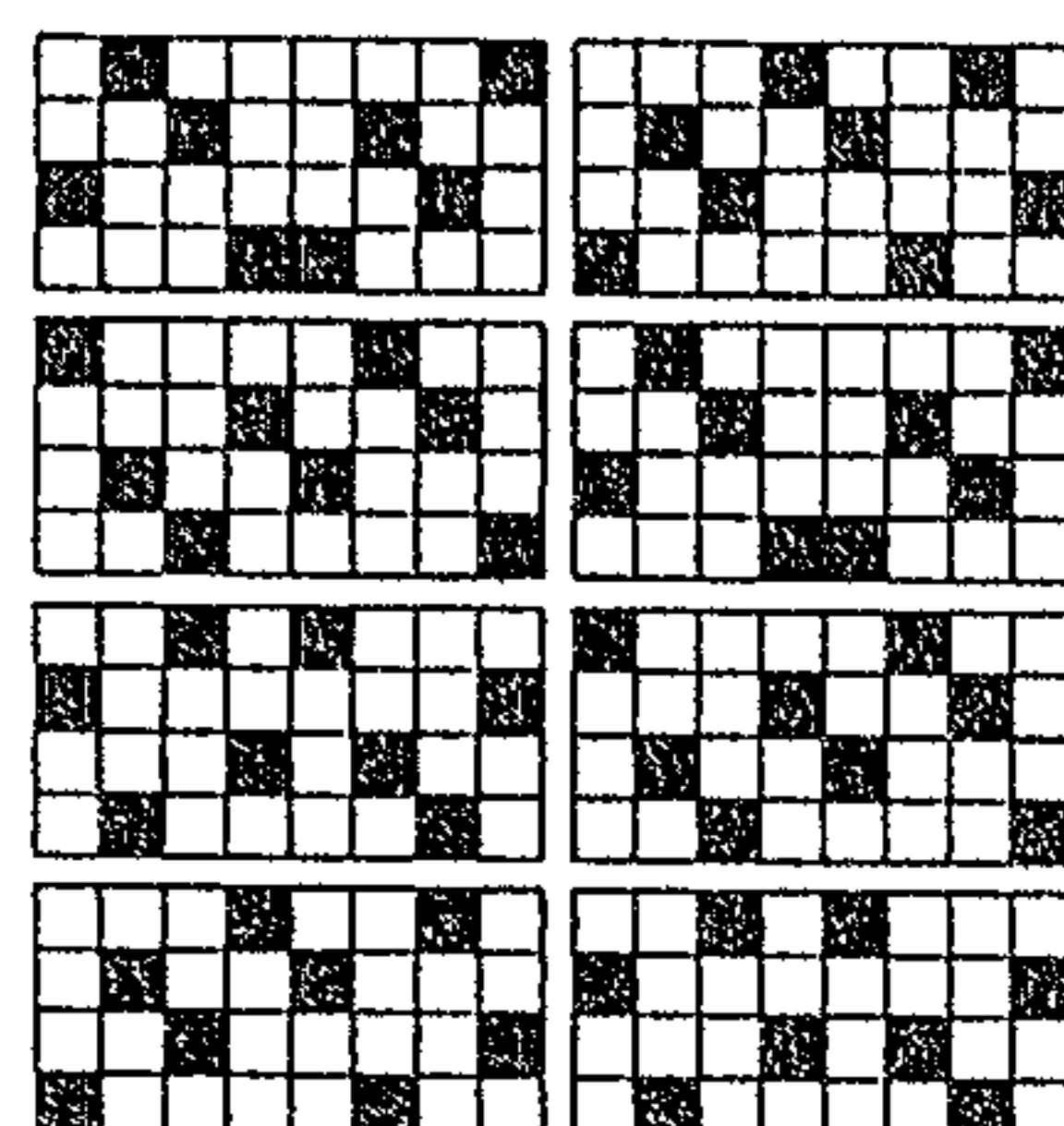


FIG. 11G

3rd-pass

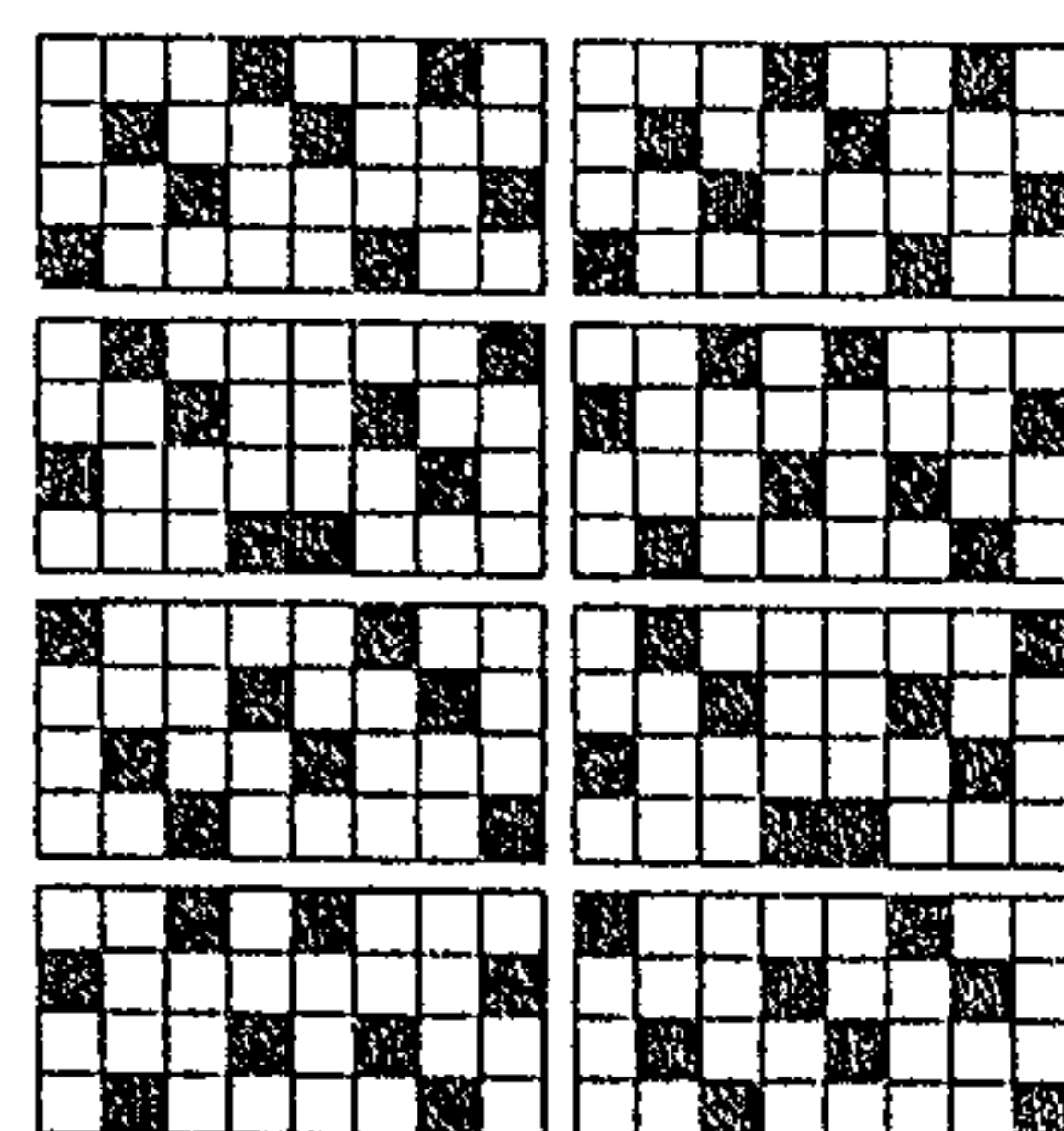


FIG. 11H

4th-pass

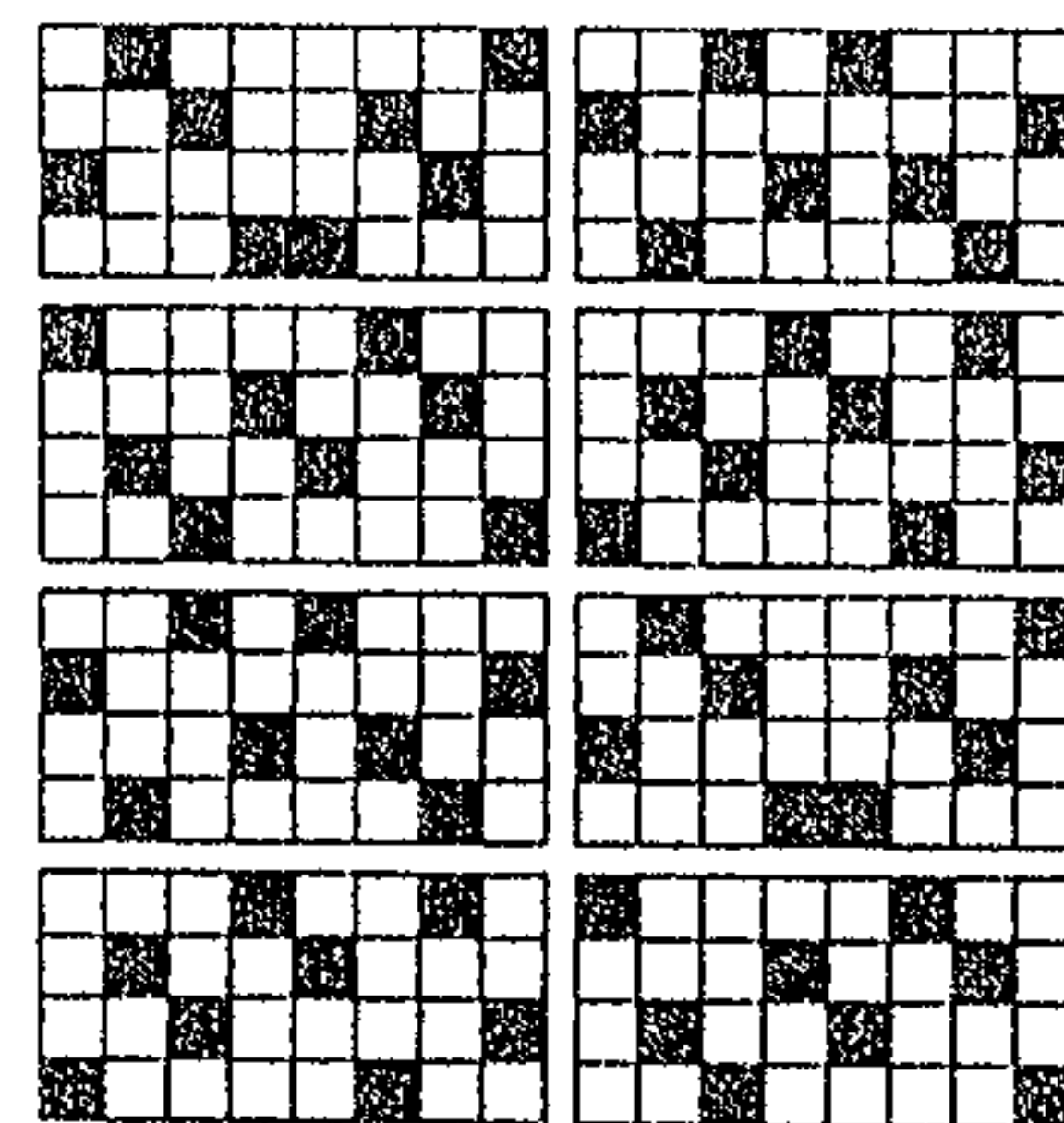


FIG. 12A

1st-pass

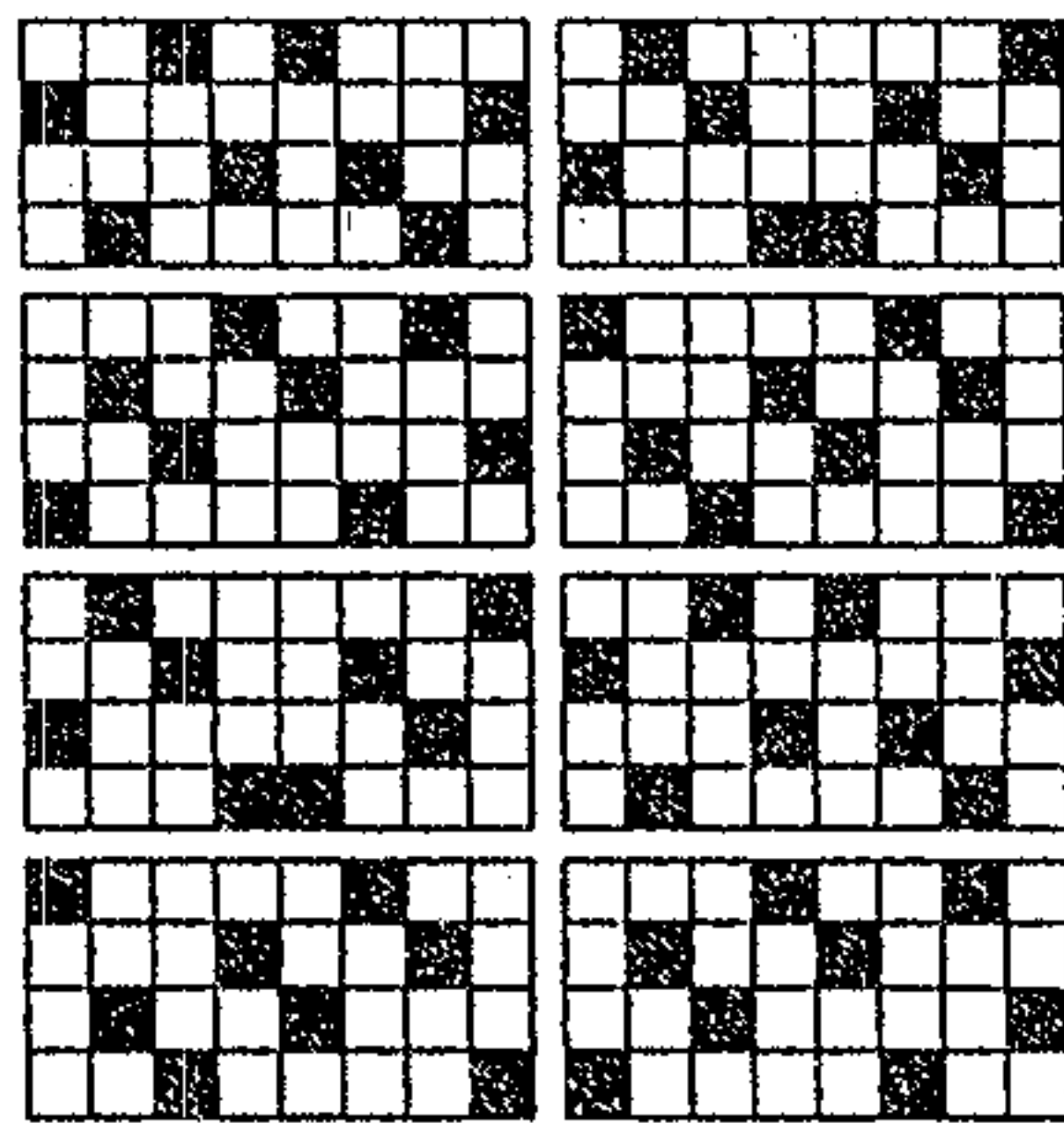


FIG. 12B

2nd-pass

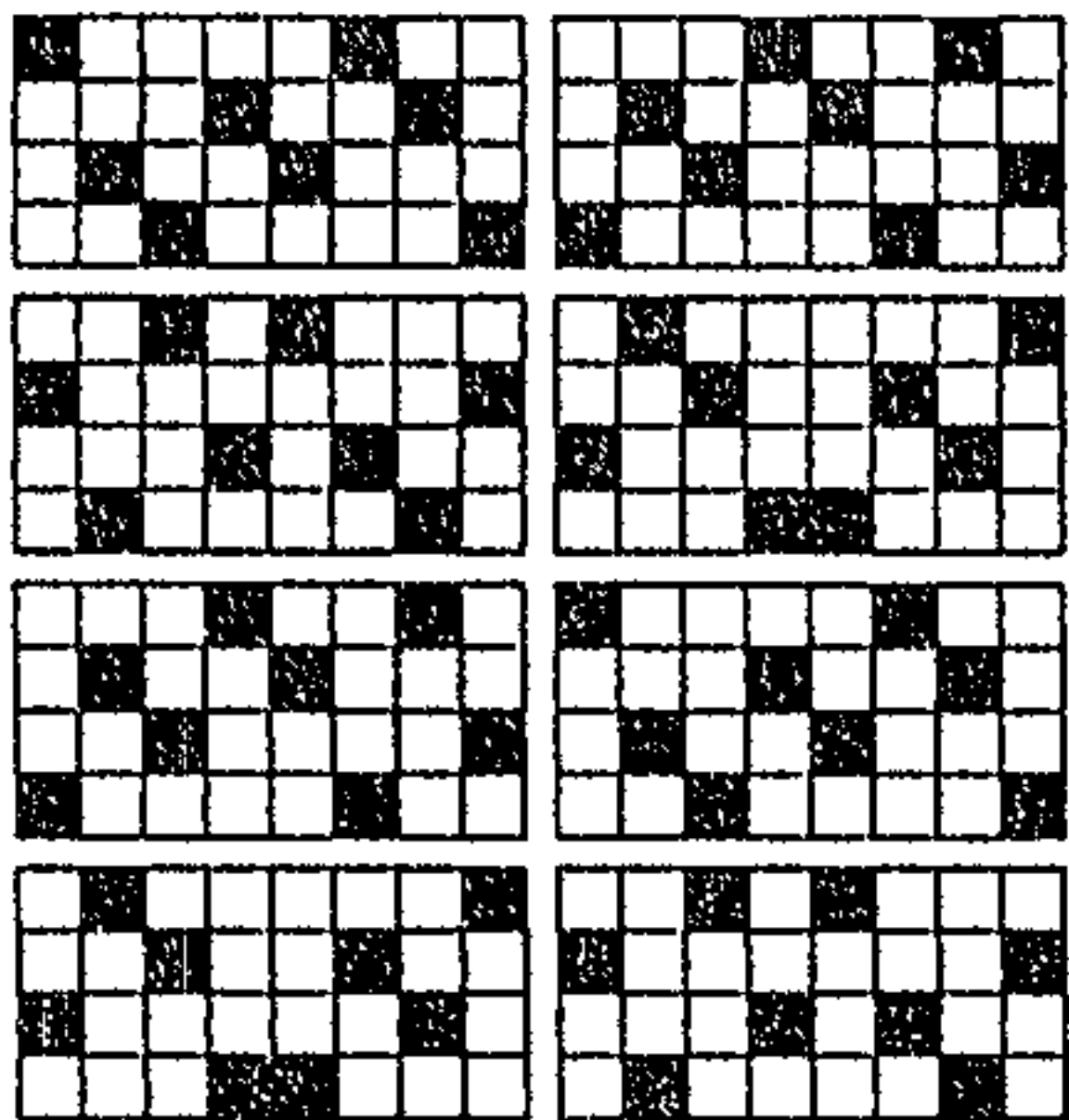


FIG. 12C

3rd-pass

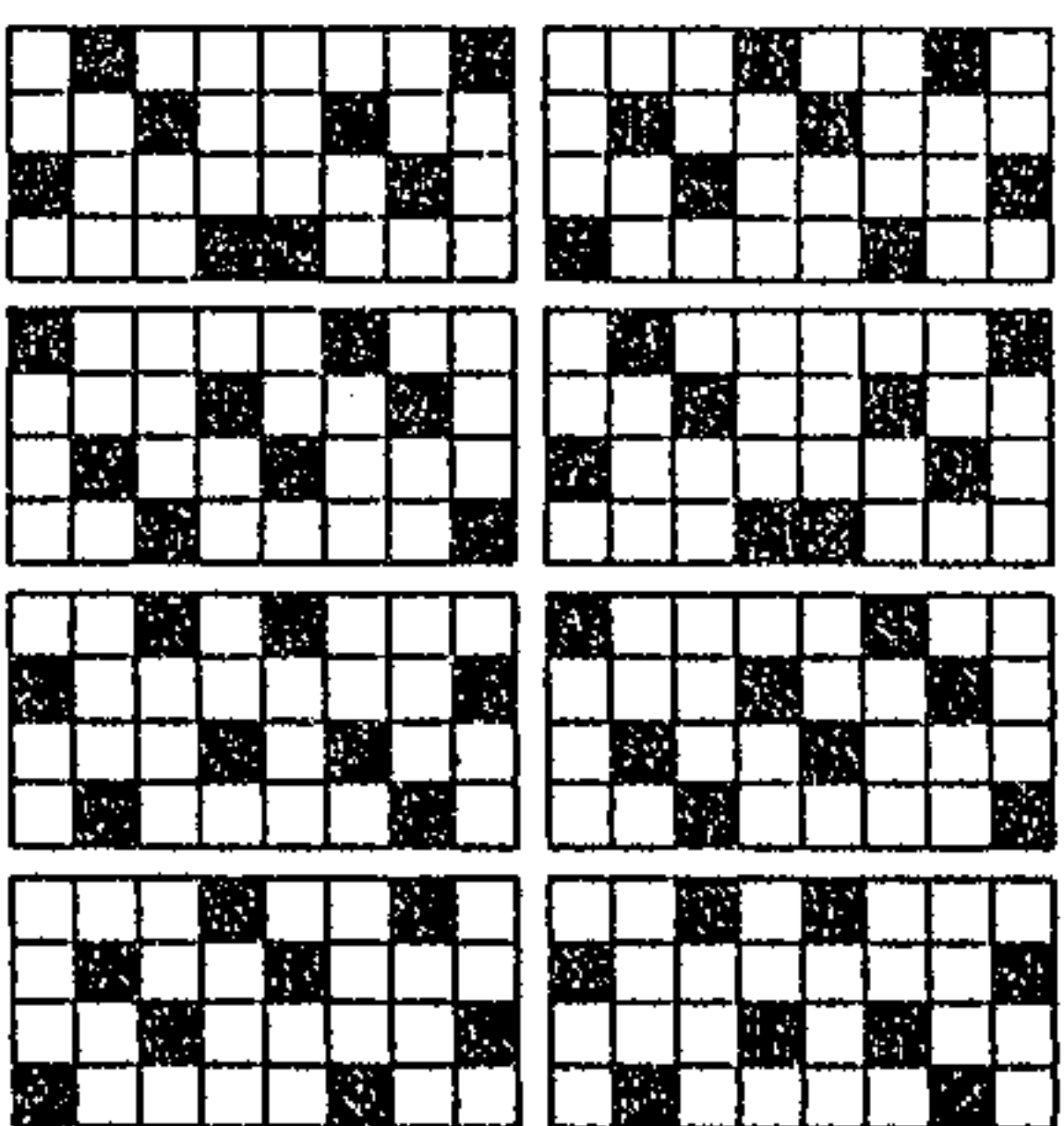
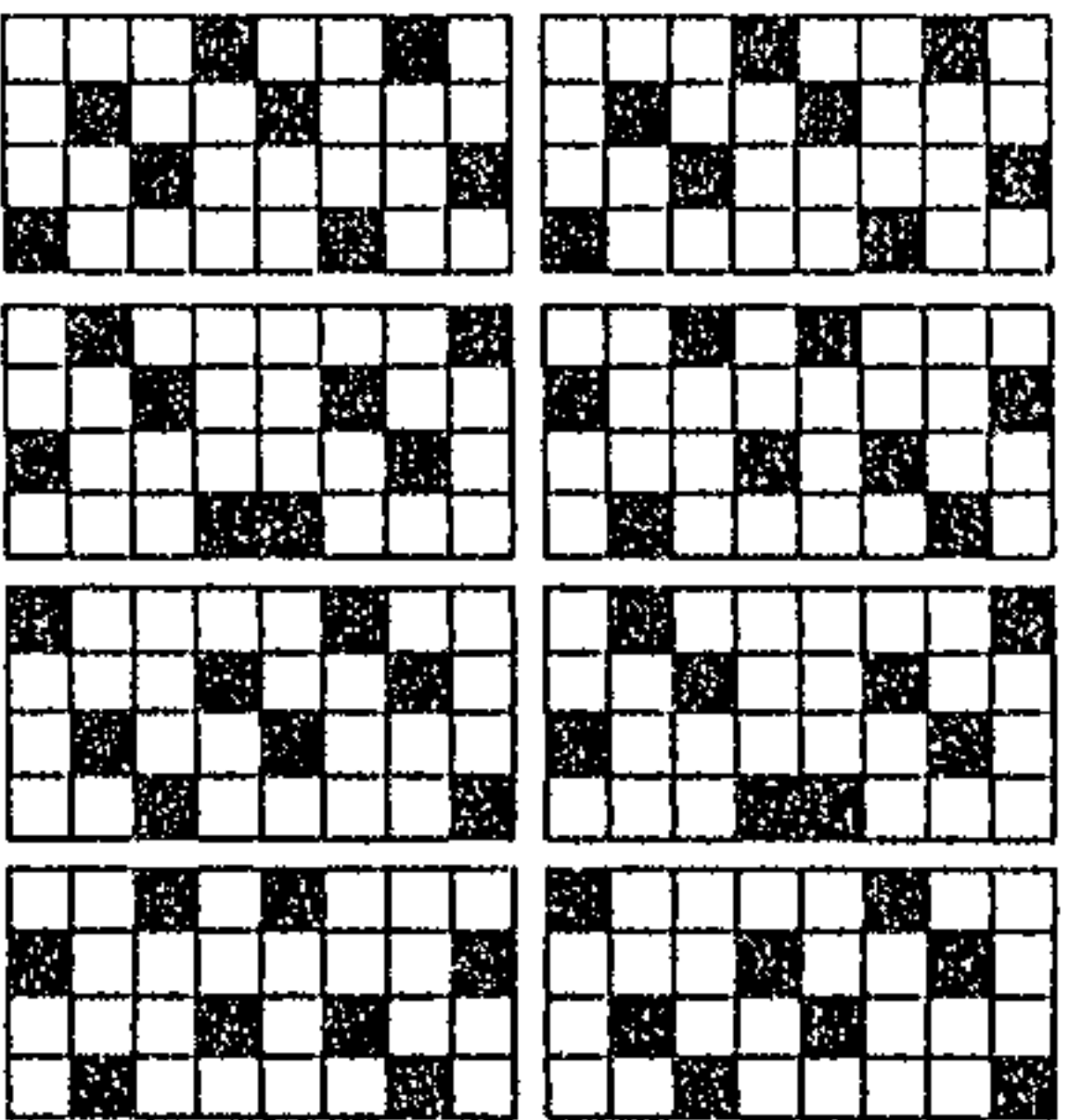


FIG. 12D

4th-pass



M

FIG. 12E

1st-pass

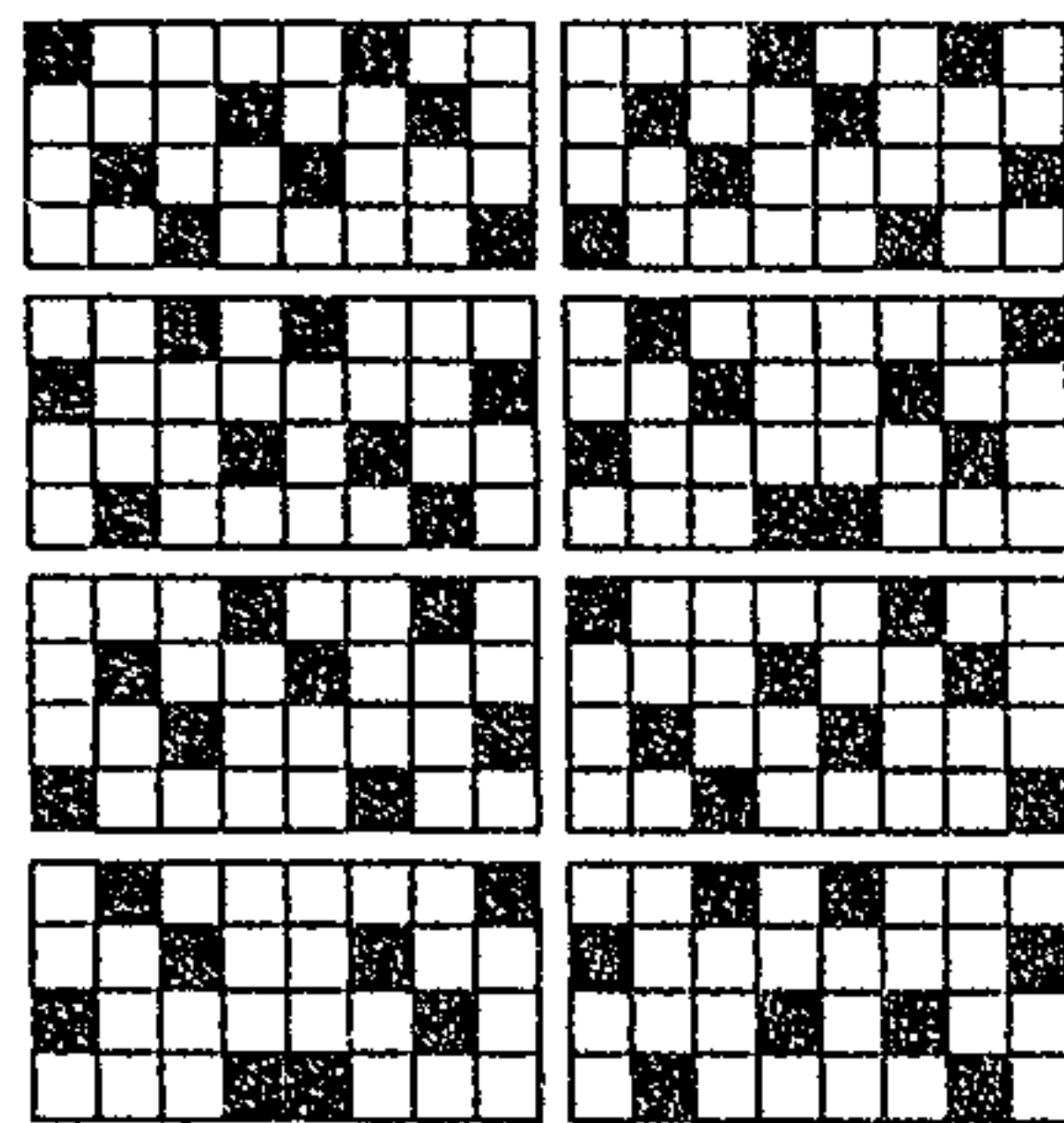


FIG. 12F

2nd-pass

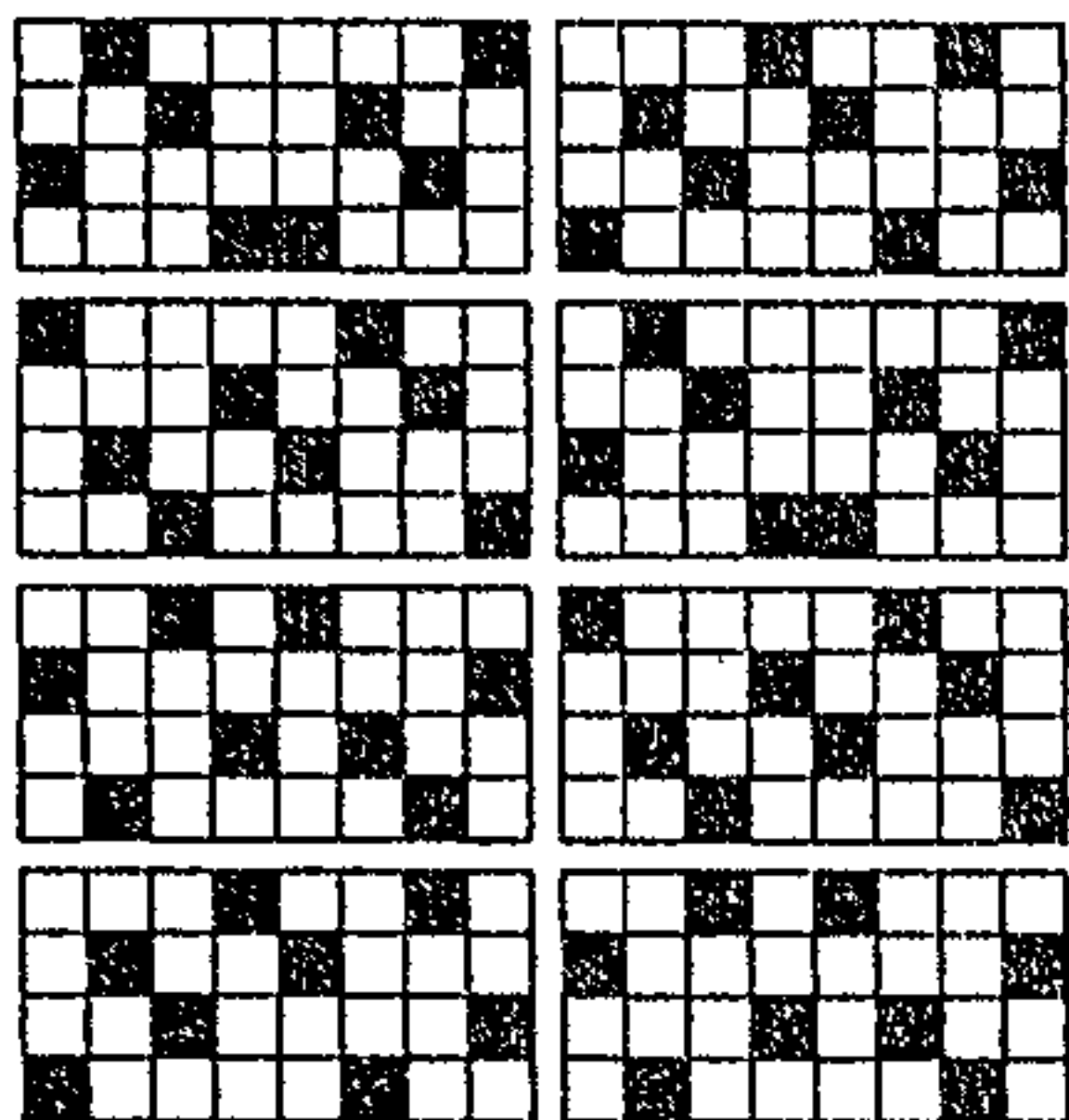


FIG. 12G

3rd-pass

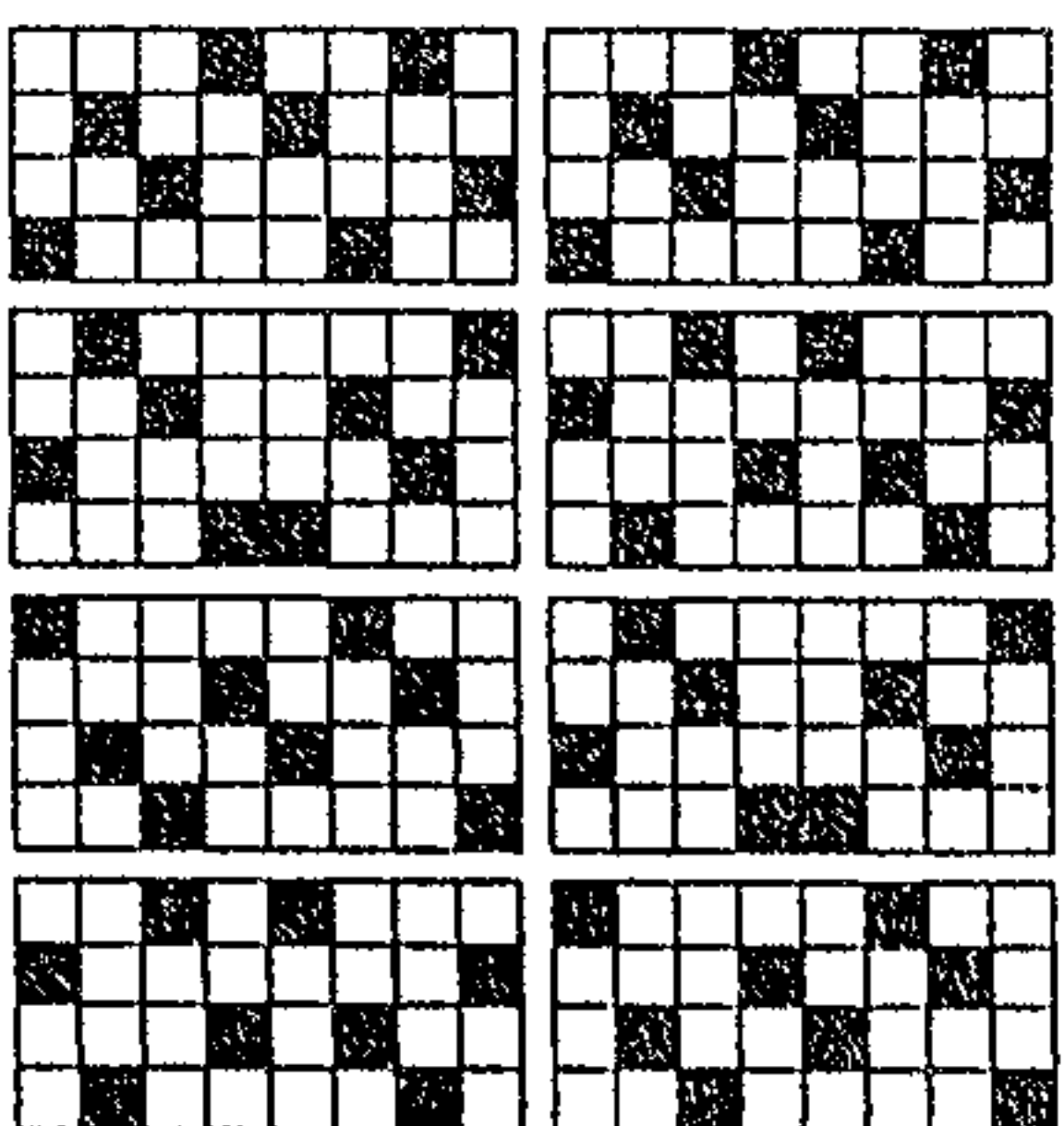
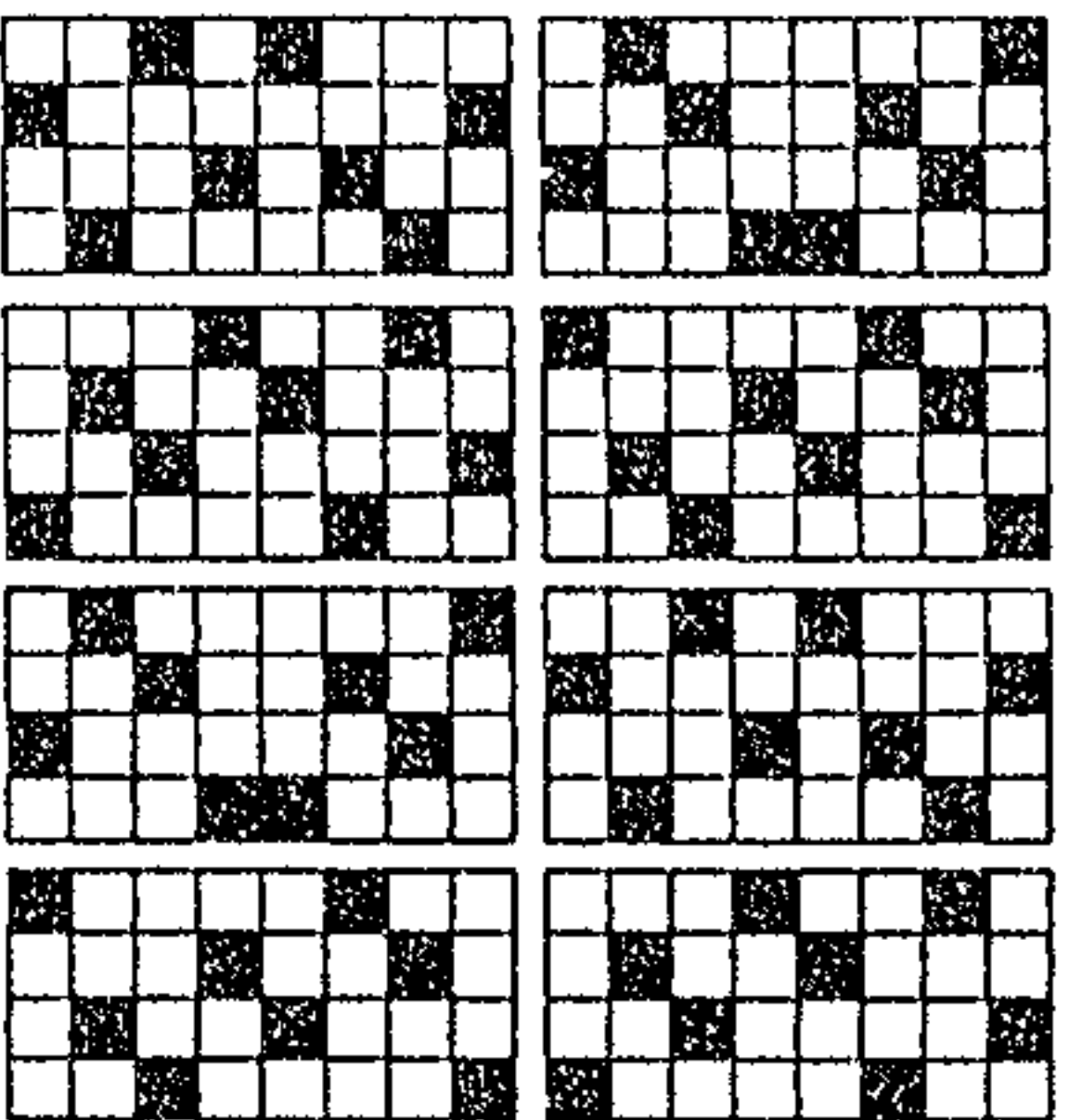


FIG. 12H

4th-pass



Y

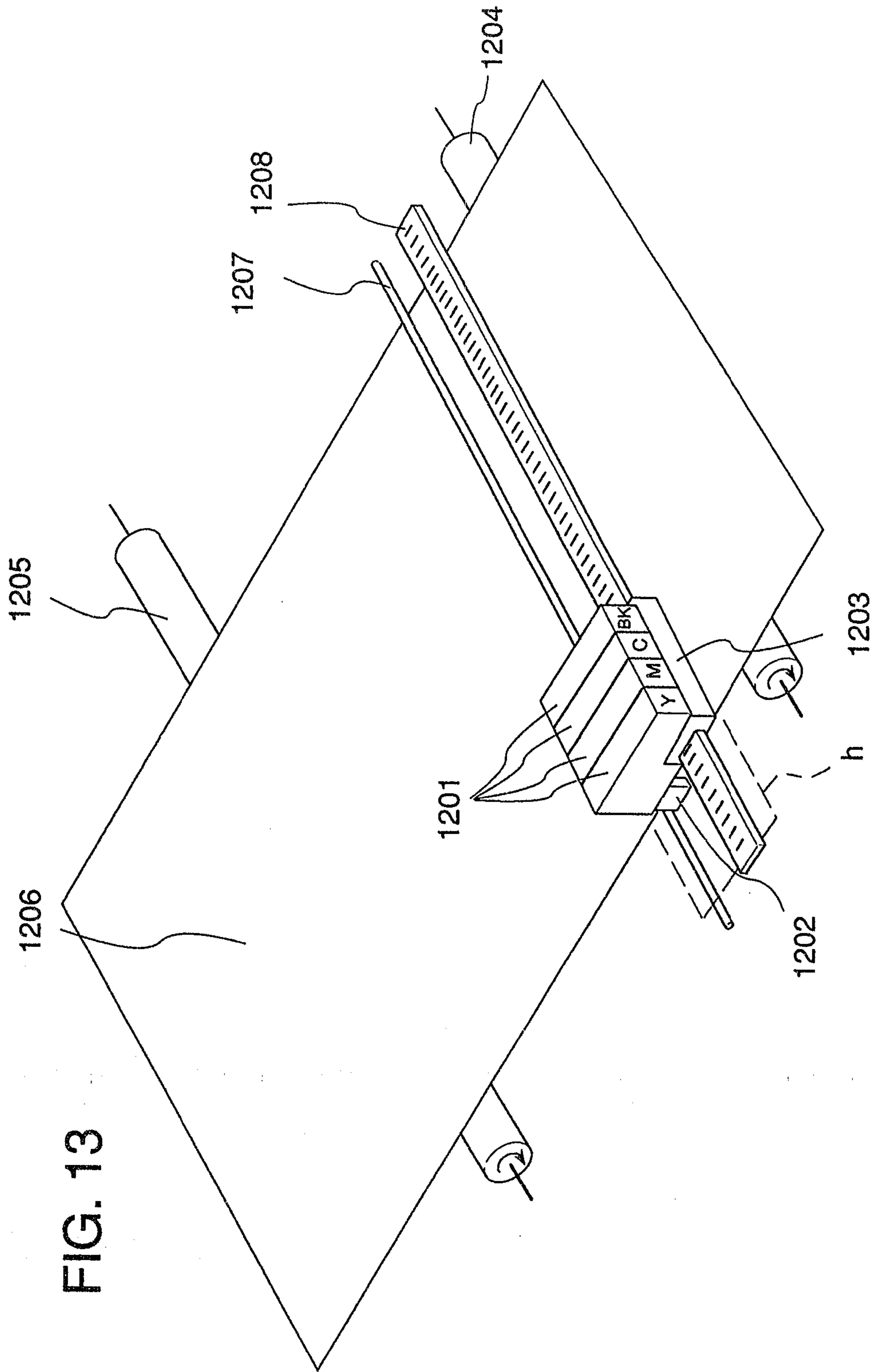


FIG. 13

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FIG. 14A

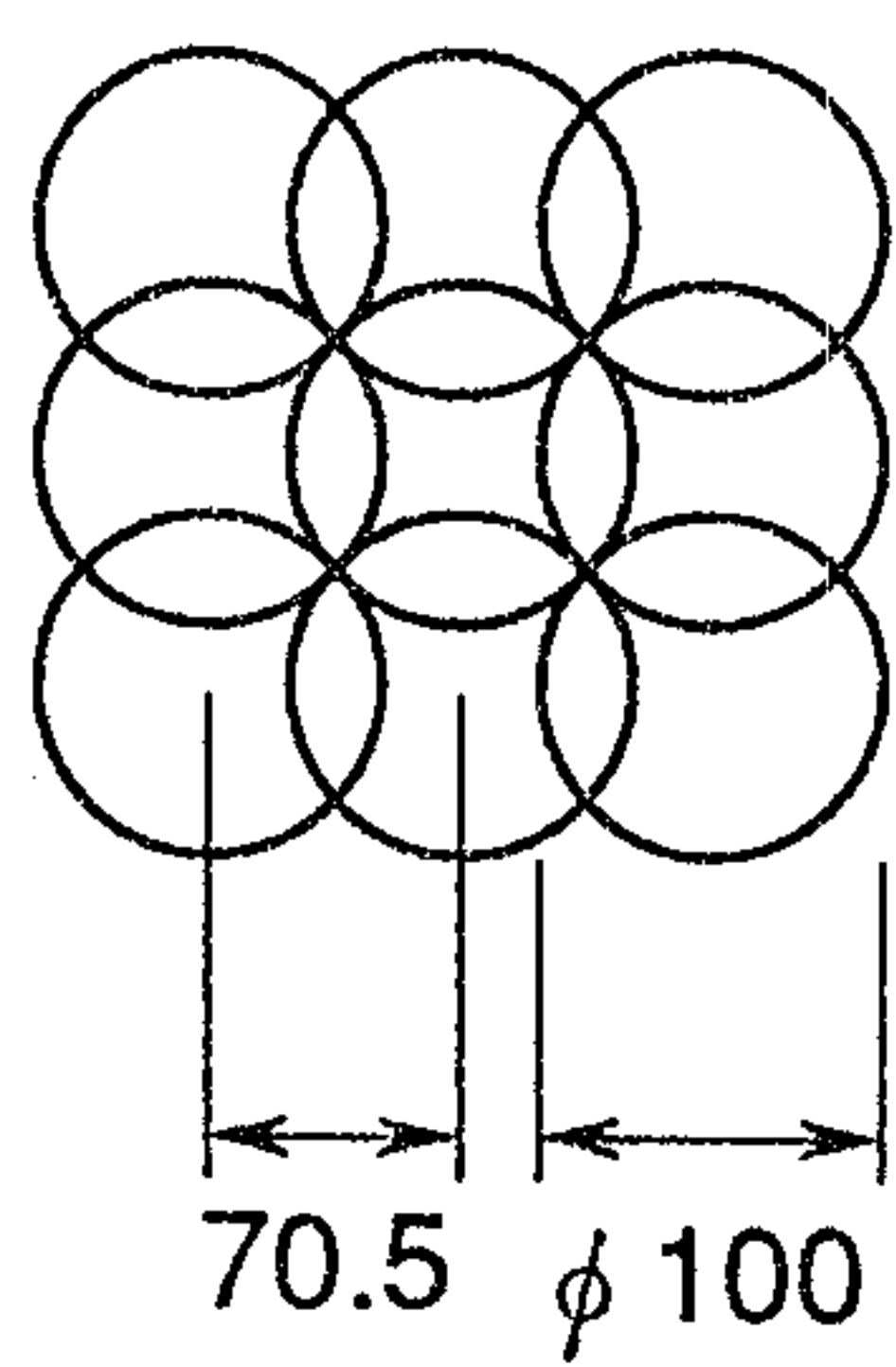


FIG. 14B

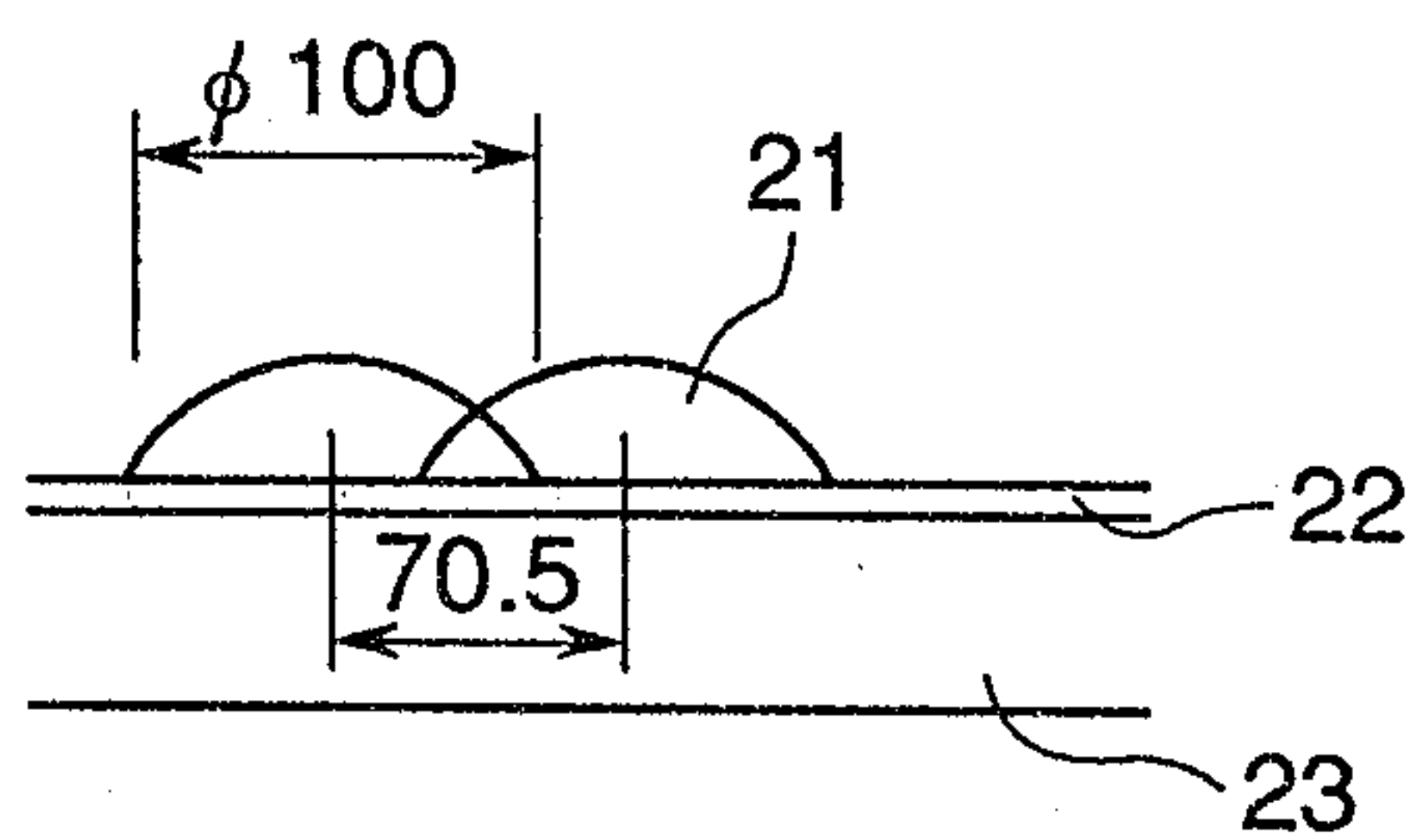


FIG. 15A

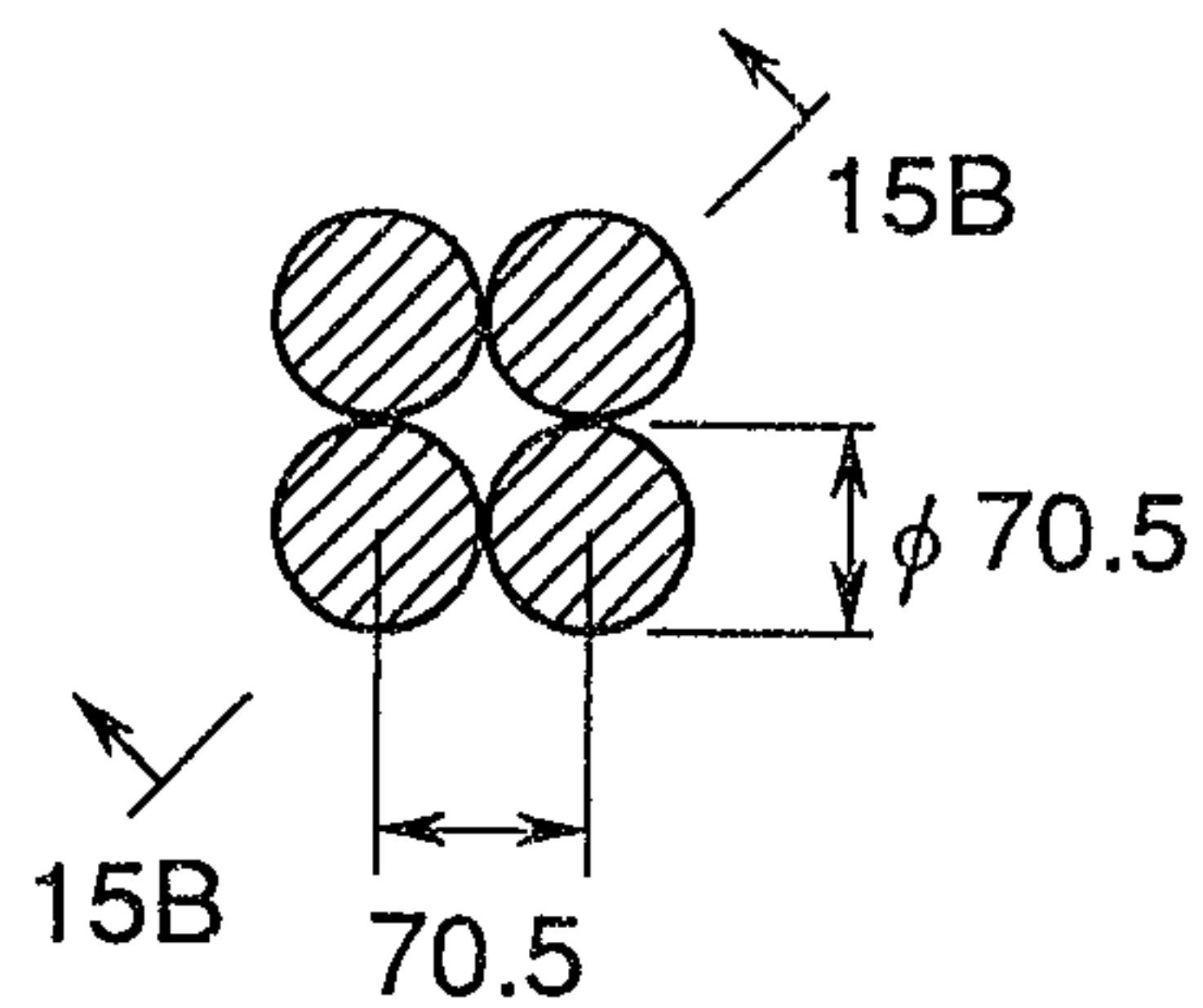


FIG. 15B

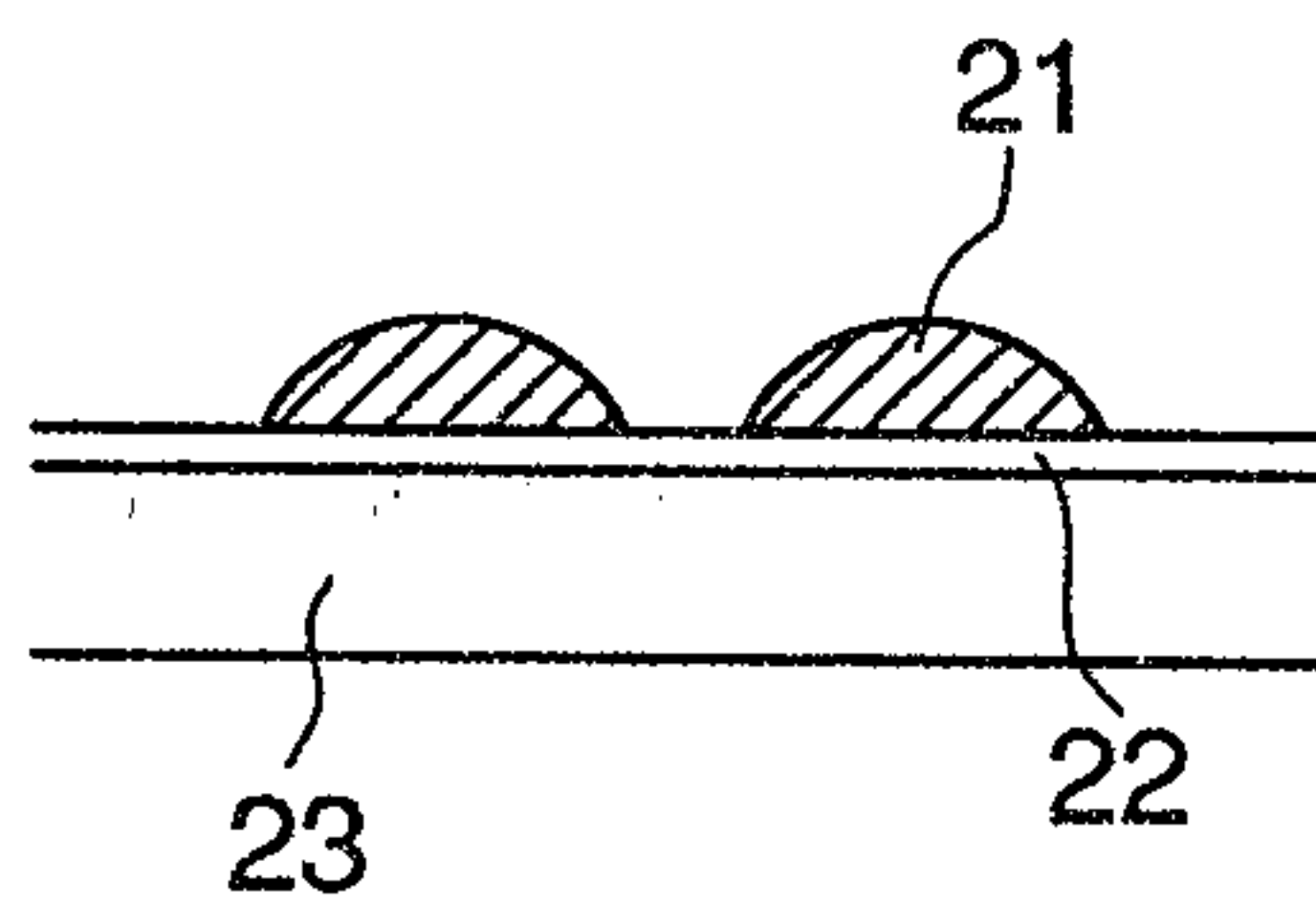


FIG. 16A

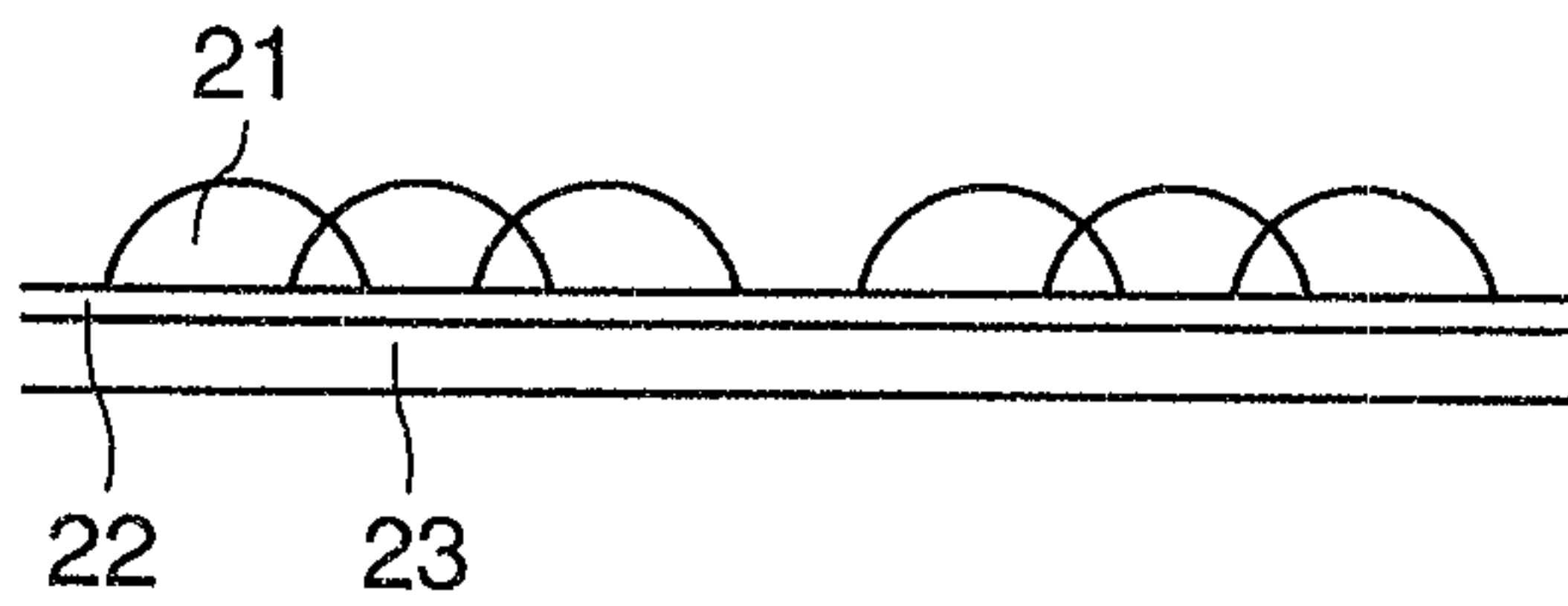


FIG. 16E

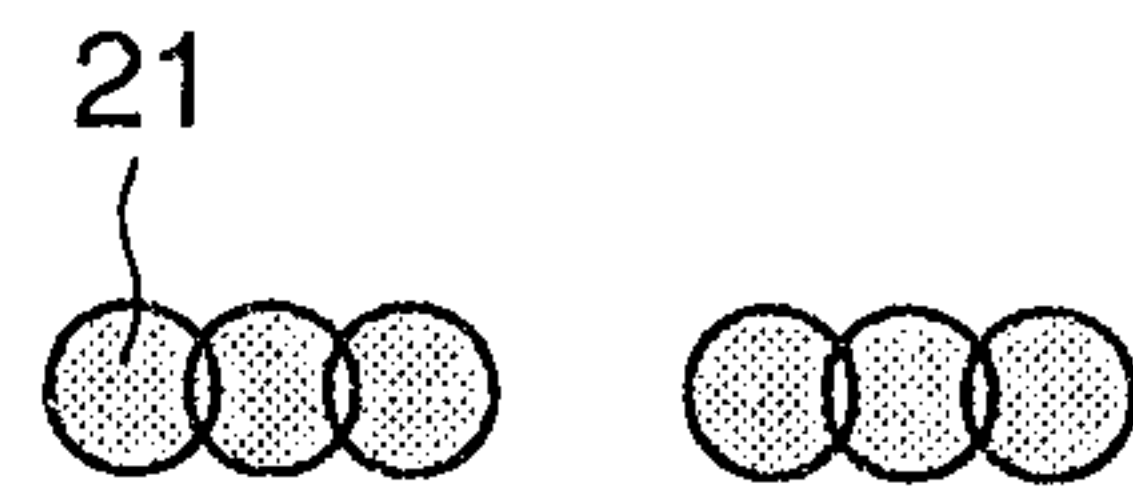


FIG. 16B

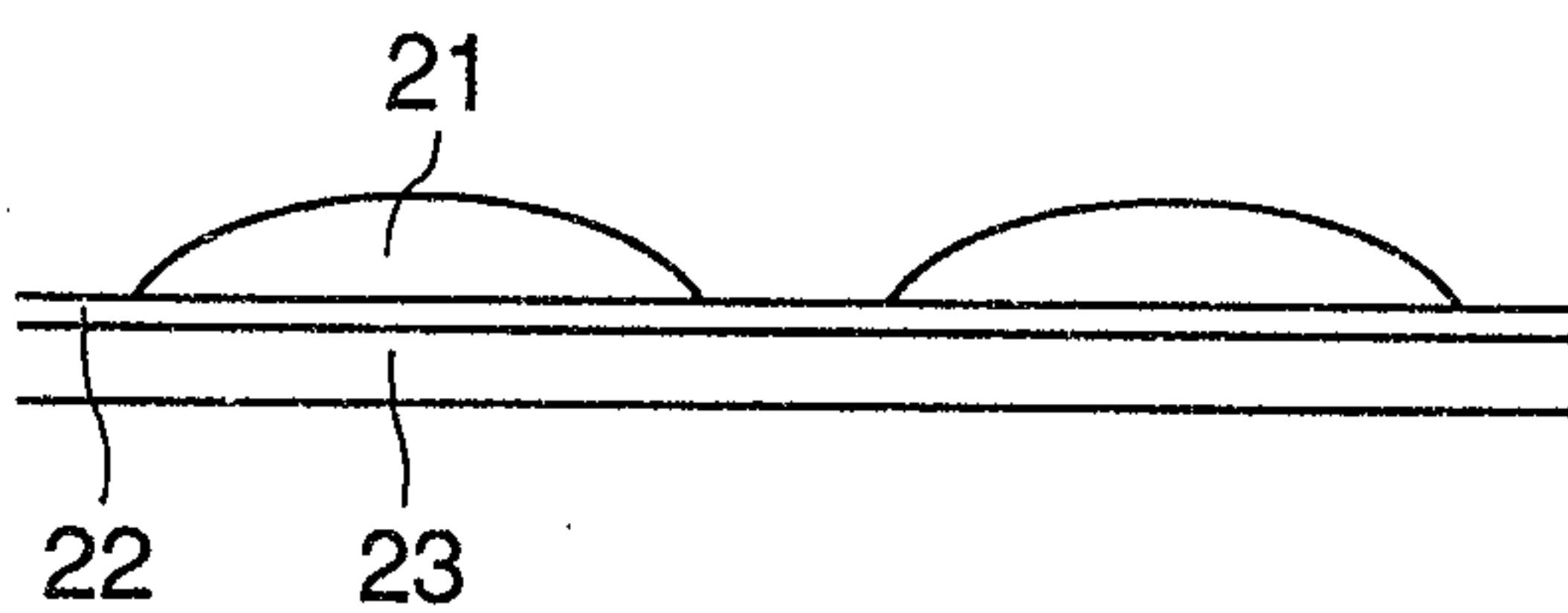


FIG. 16F



FIG. 16C

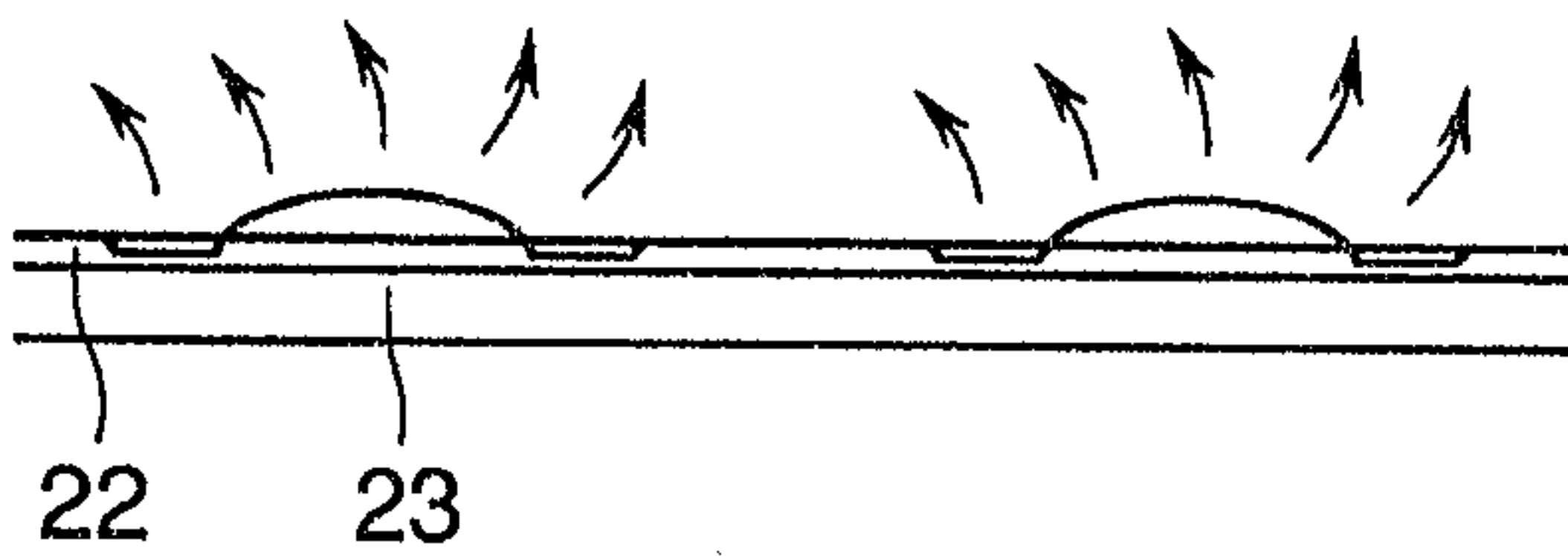


FIG. 16G



FIG. 16D

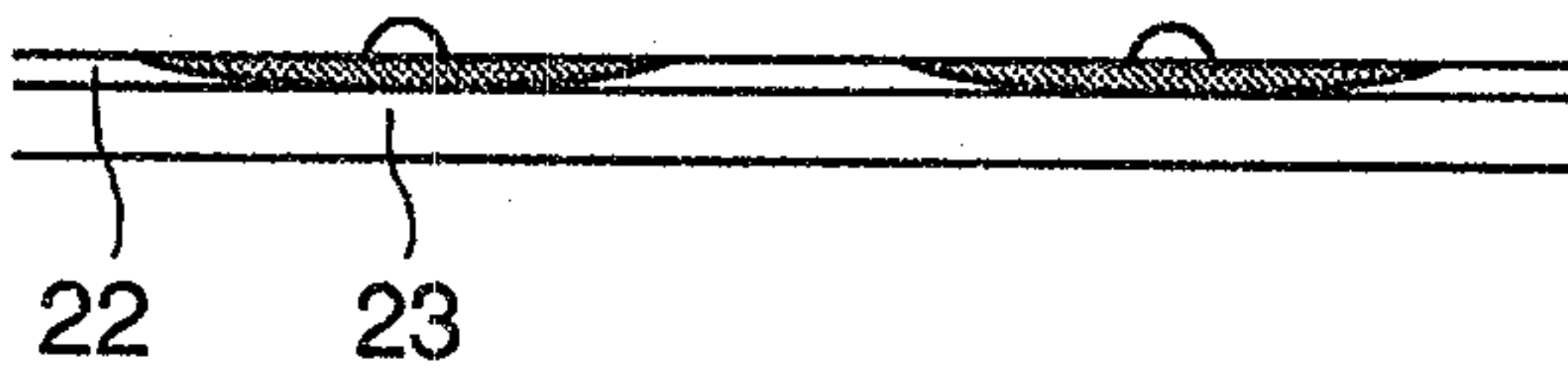


FIG. 17A

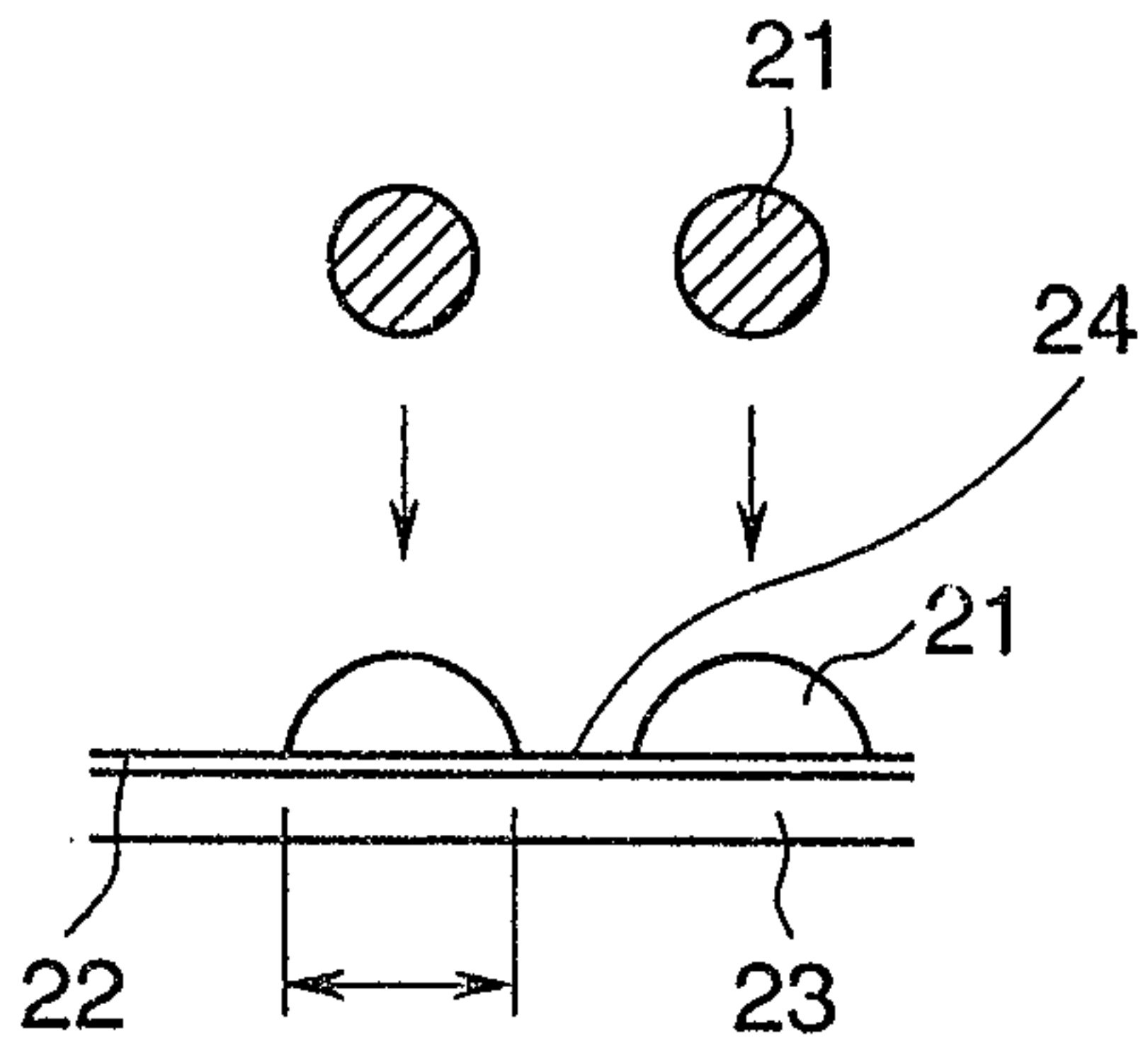


FIG. 17C



FIG. 17B

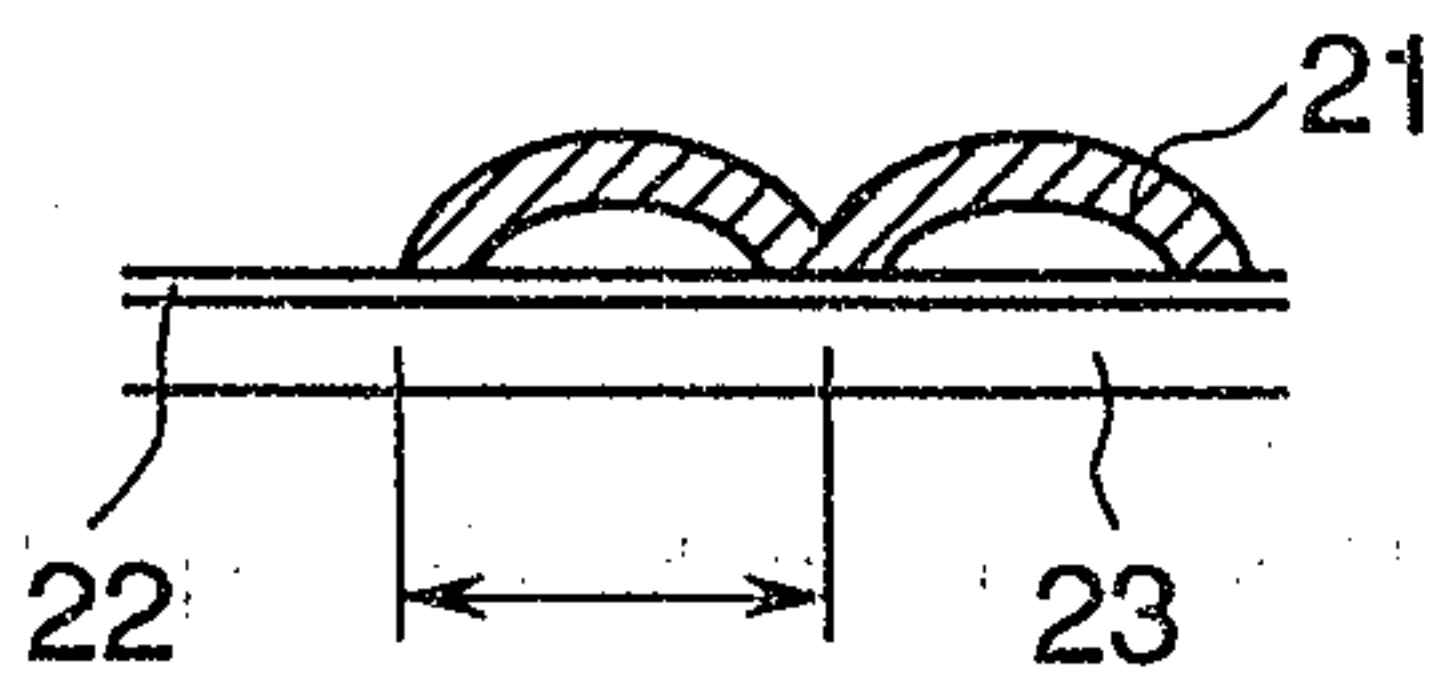


FIG. 17D

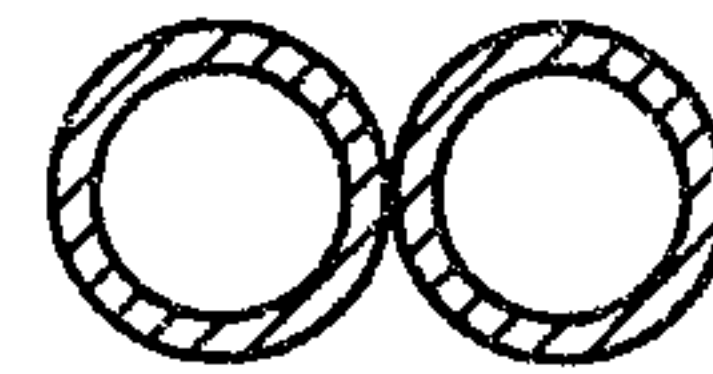


FIG. 18A

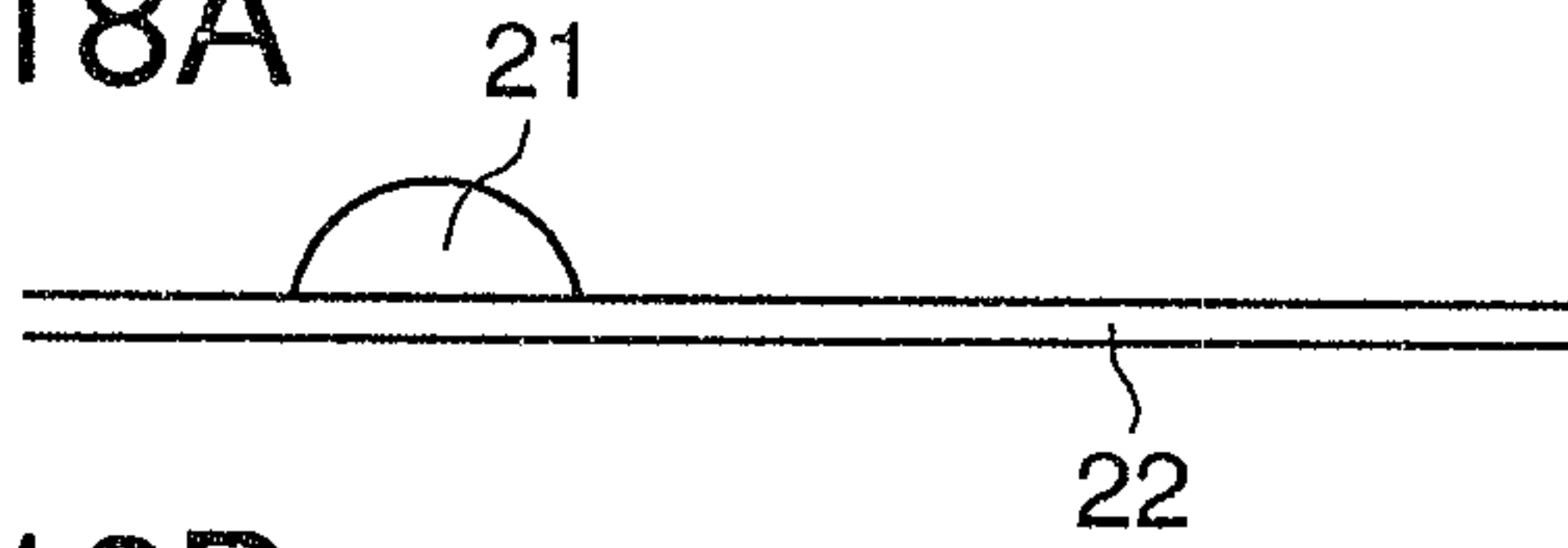


FIG. 18B

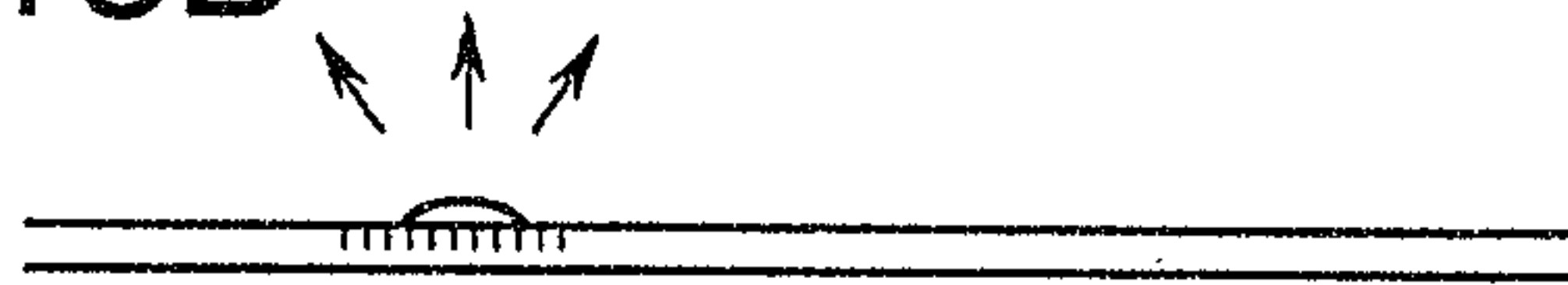


FIG. 18C

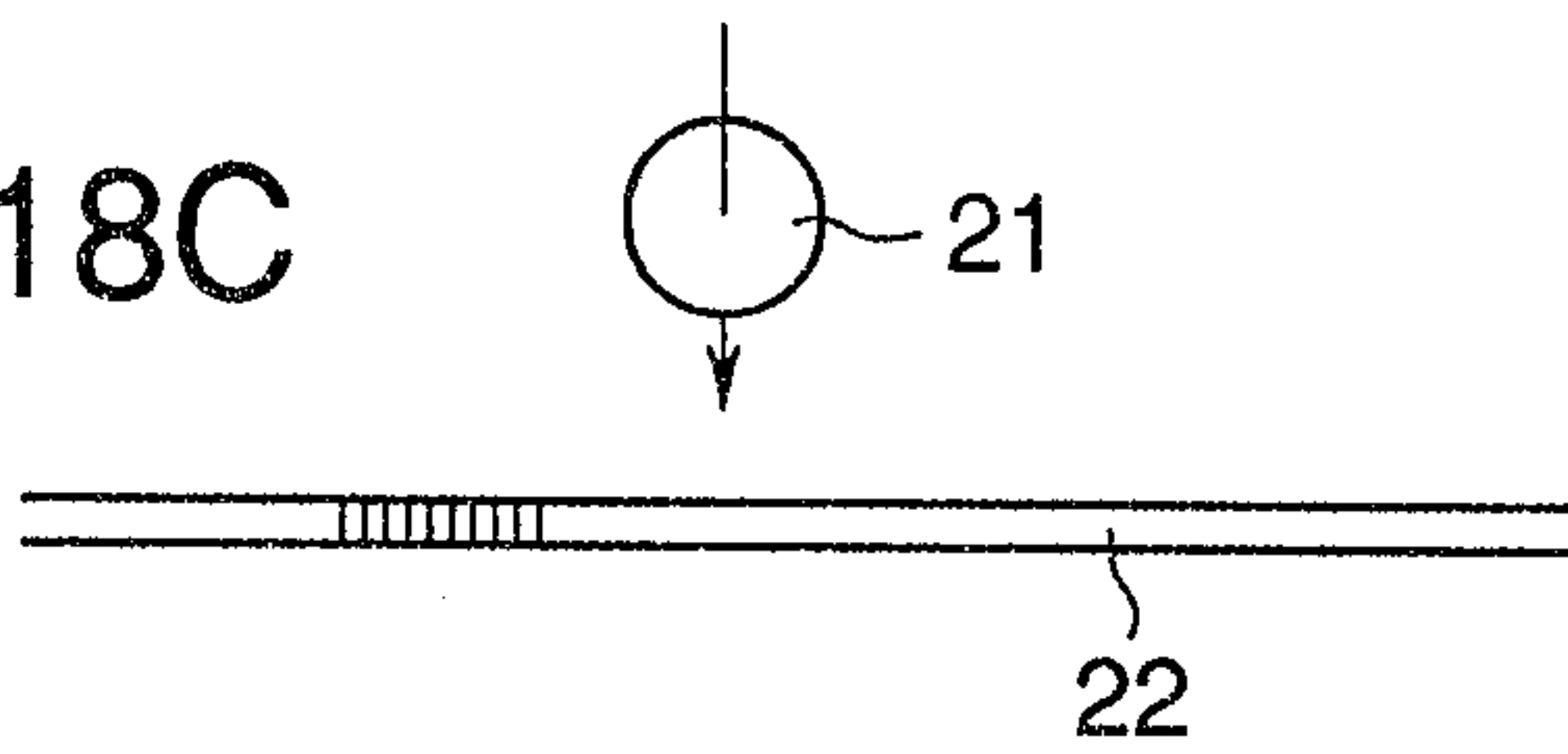


FIG. 18D



FIG. 18E

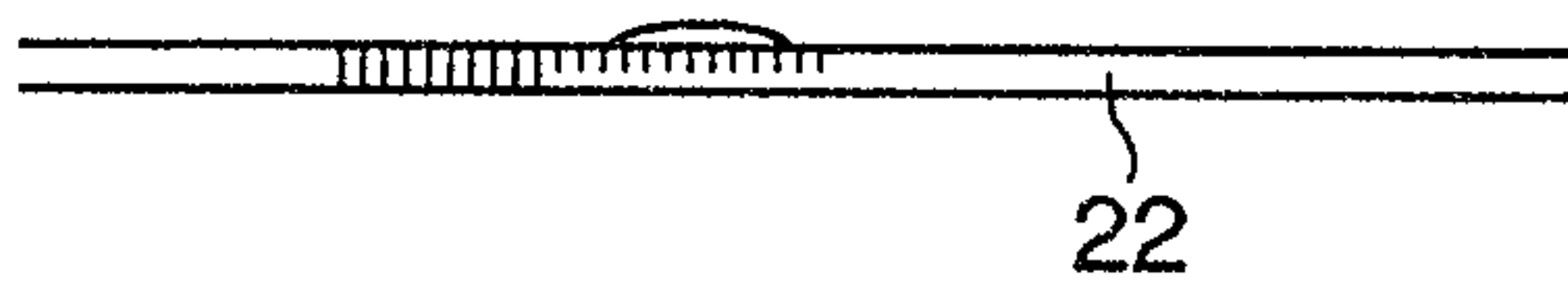


FIG. 18F

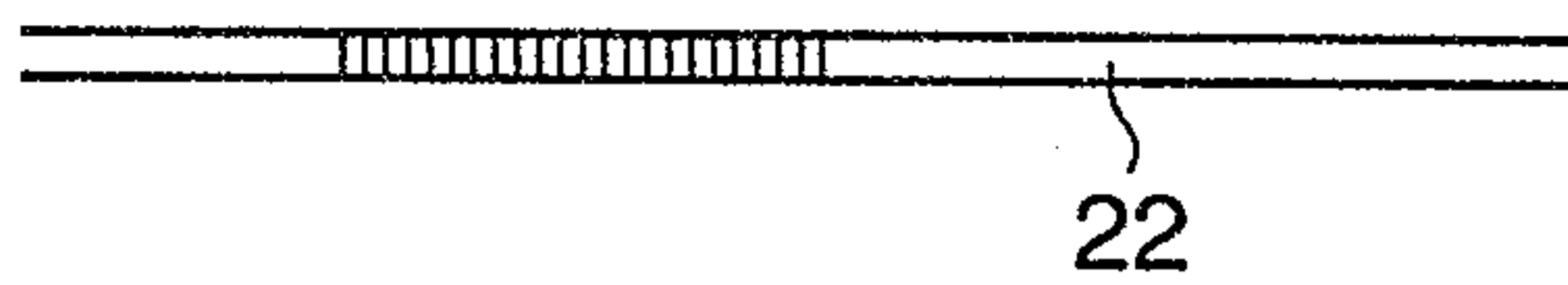


FIG. 18G



FIG. 18H



FIG. 18I



FIG. 18J

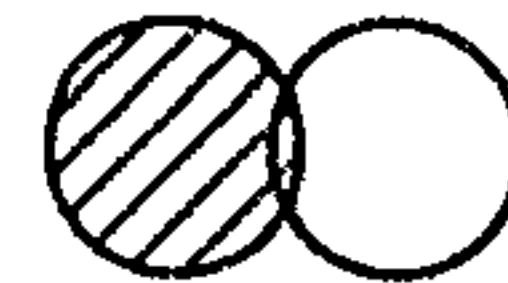


FIG. 18K



FIG. 18L



FIG. 19A

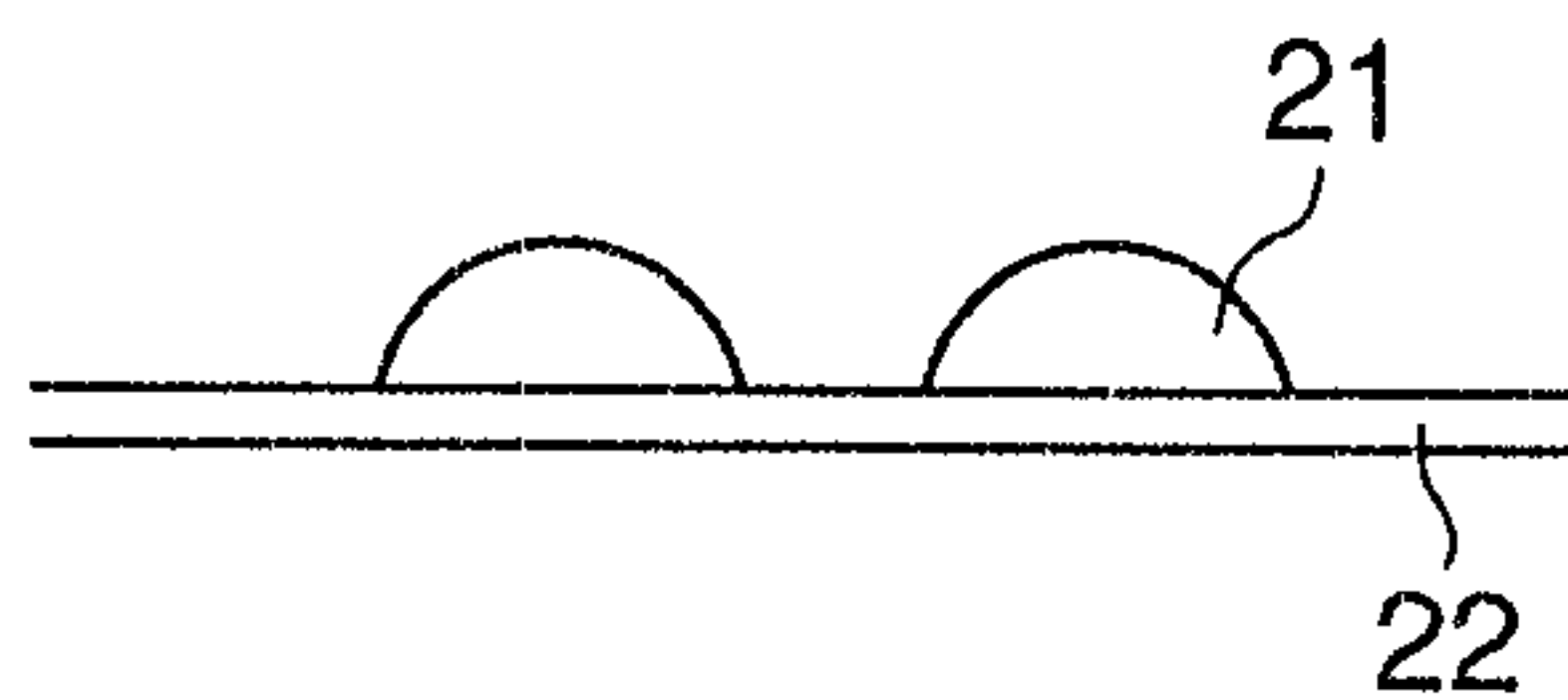


FIG. 19B

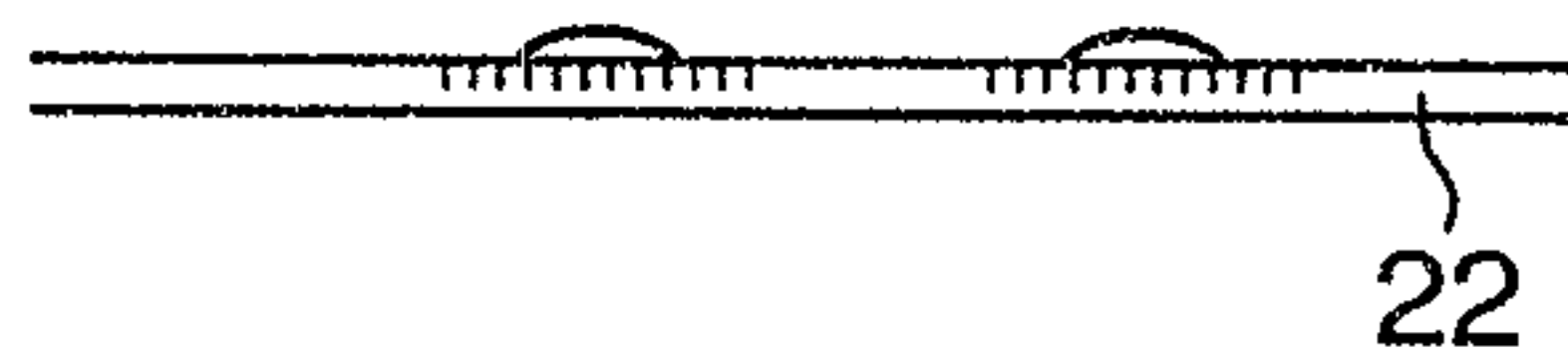


FIG. 19C

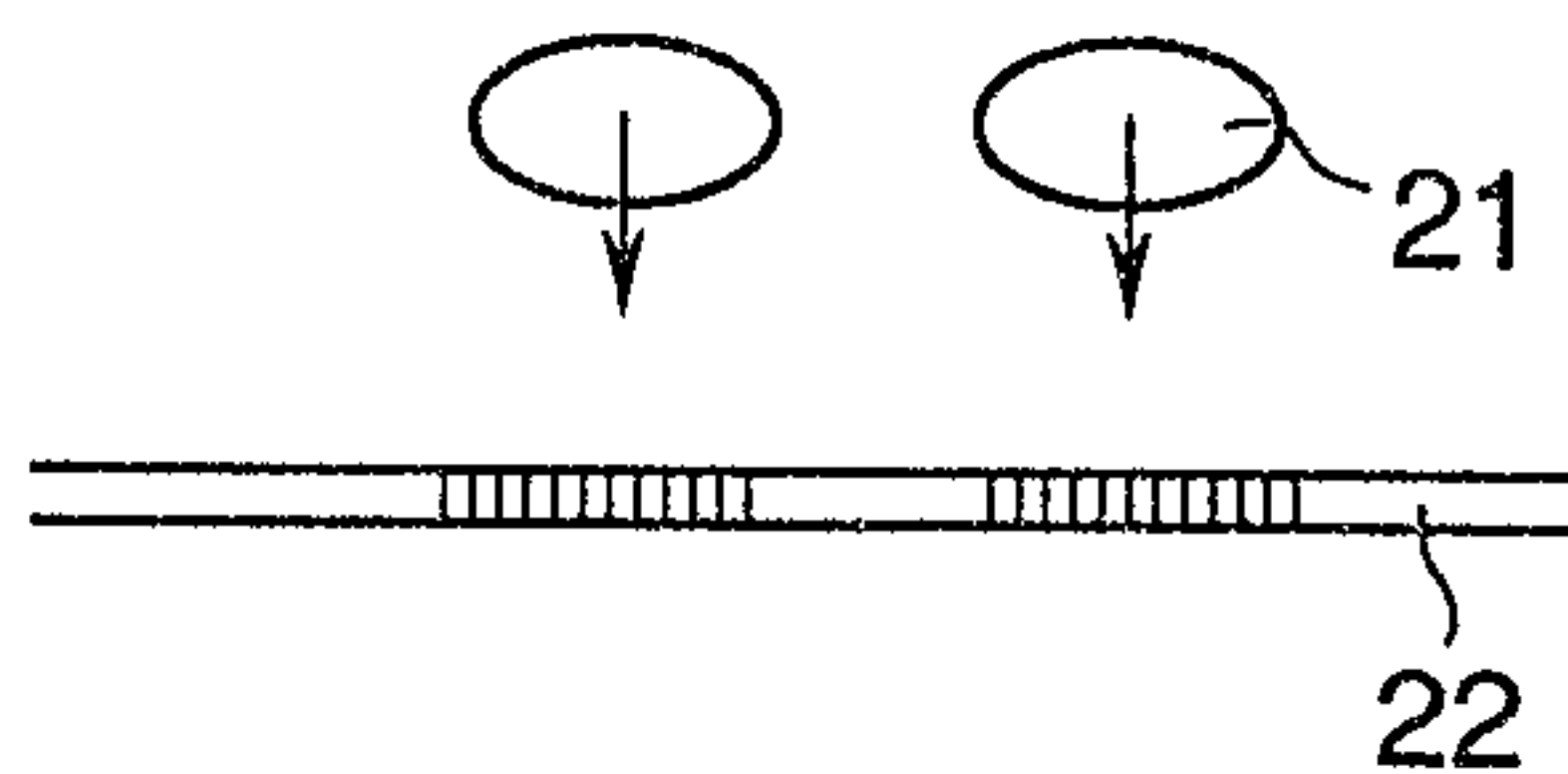


FIG. 19D

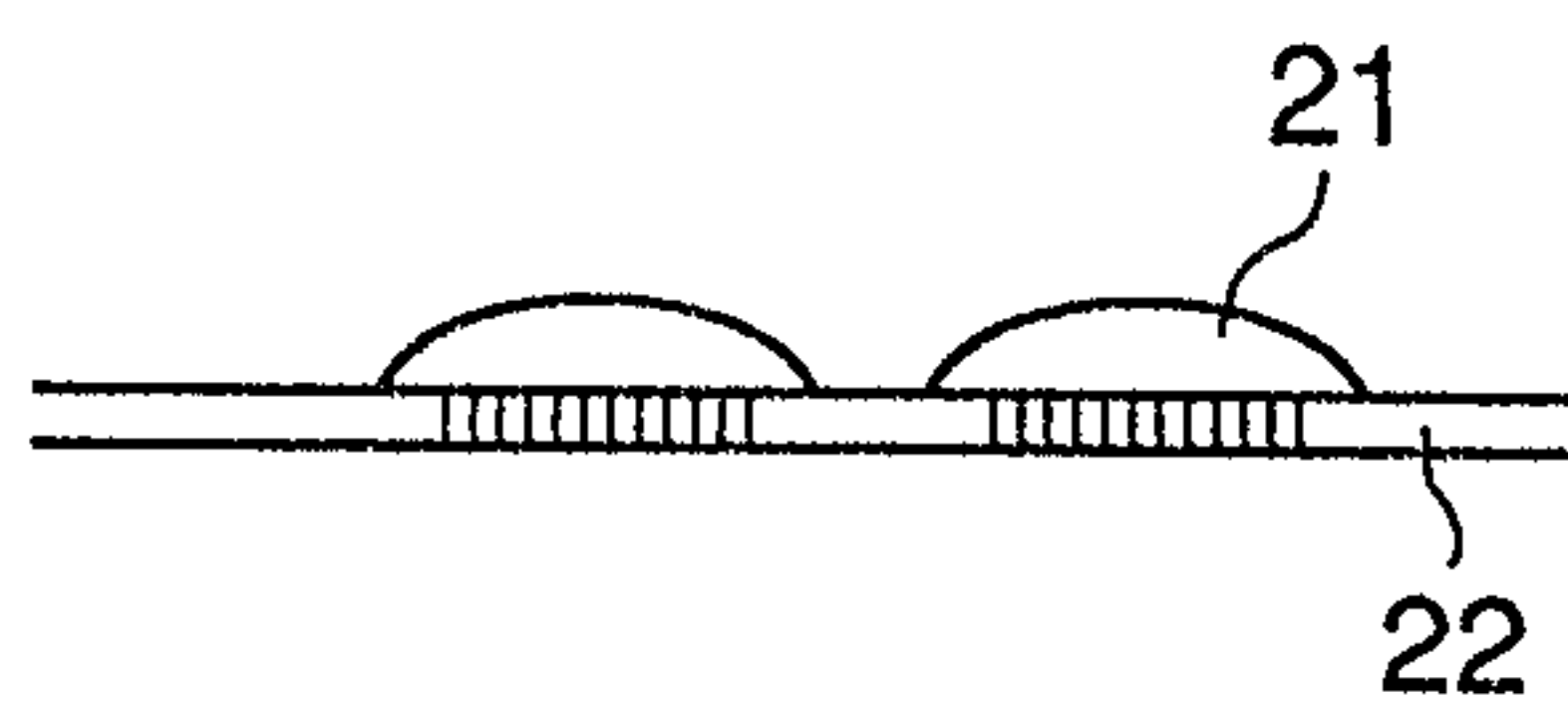


FIG. 19E

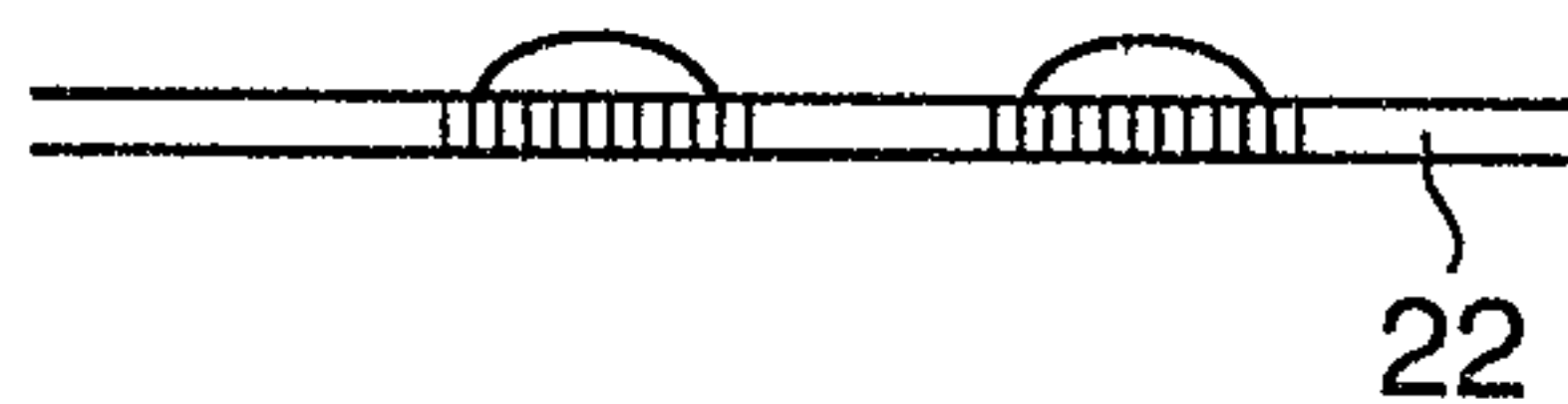


FIG. 19F

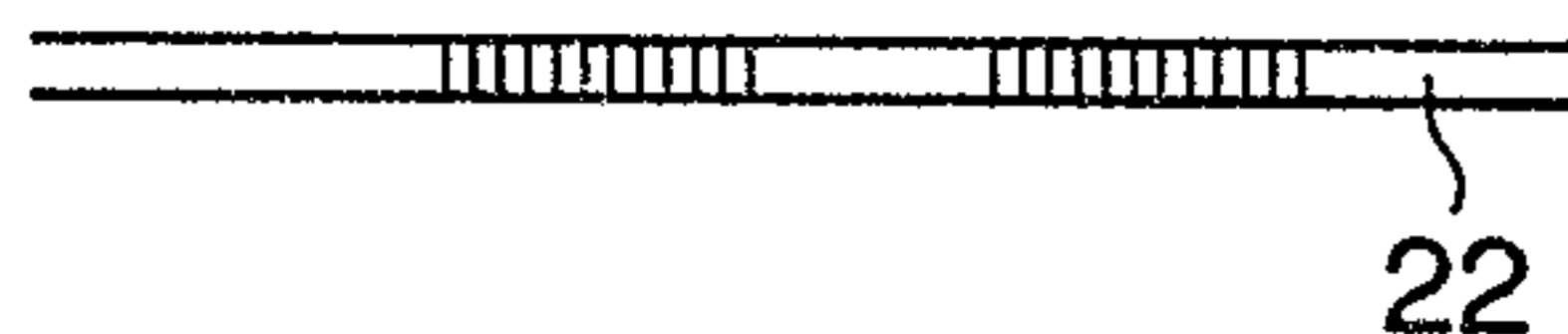


FIG. 20

