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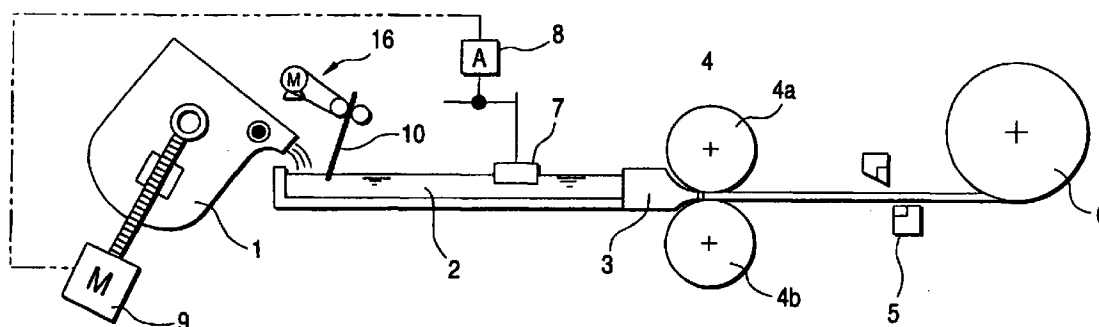
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(54) **Method for producing planographic printing plate support**

(57) In a method for producing a planographic printing plate support, aluminum is melted, molten aluminum is supplied a gap between a pair of cooling rolls from a molten metal supply nozzle, at least one of cold rolling and heating at least once to form an aluminum thin plate having a thickness in a range of from 0.1 mm to 0.5 mm, and the aluminum thin plate is corrected to form an aluminum support and roughen a surface of the aluminum

support. The molten metal supply nozzle has an inner surface which is brought into contact with the molten metal and which is coated with aggregate particles having a particle size distribution with a median size in a range of from 5 μm to 20 μm and a mode size in a range of from 4 μm to 40 μm to thereby cast and roll plate-like aluminum continuously.

FIG. 1



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Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0001] The present invention relates to a method for producing a planographic printing plate aluminum support by using a twin-roll continuous casting method. Particularly, the present invention relates to a method for producing a planographic printing plate aluminum support which is good in surface quality so that stripe-like surface-quality defects can be prevented from being generated in an aluminum plate continuously or intermittently in its rolling direction.

2. Description of the Related Art

[0002] An aluminum plate (including an aluminum alloy plate) is used as a printing plate aluminum support, especially, as an offset printing plate support.

[0003] Generally, in order to use an aluminum plate as an offset printing plate support, the aluminum plate is required to have both moderate attaching property and moderate water retention property with respect to a light-sensitive material.

[0004] Accordingly, the surface of the aluminum plate must be roughened to have uniform and fine particles. Because the surface-roughening treatment has a remarkable influence on both the printing performance and printing endurance of the plate material when offset printing is actually performed after plate making, the quality of the surface-roughening treatment becomes an important factor for production of the plate material.

[0005] An AC electrolytic etching method is generally used as a method for roughening the surface of the printing plate aluminum support. As an electric current, an ordinary sinusoidal alternating current or a special alternating-waveform current such as a rectangular-wave current or the like is used. Further, a suitable electrode made from graphite or the like was used as a counter electrode so that the surface of the aluminum plate was roughened by an alternating current. The treatment was generally performed by one step and the pit depth obtained therein was shallow as a whole, so that printing endurance was poor. Therefore, various methods have been proposed to obtain an aluminum plate adapted for a printing plate support having a grained surface in which pits each having a depth larger than its diameter exist uniformly and finely. As the methods, there are known a surface-roughening method using a special electrolytic electric source waveform (JP-A-53-67507) (hereinafter, JP-A means Unexamined Japanese Patent Publication (kokai)), the ratio of an anodic electric quantity to a cathodic one at the time of electrolytic surface-roughening by means of an alternating current (JP-A-54-65607), electric source waveform (JP-A-55-25381), combination of the quantity of current conduction per unit area (JP-A-56-29699), etc.

[0006] Further, combination with mechanical surface roughening (JP-A-55-142695), etc. is known.

[0007] On the other hand, in the method for producing an aluminum support, an ingot of aluminum is melted and held so that a slab (thickness: 400 to 600 mm; width: 1000 to 2000 mm; and length: 2000 to 6000 mm) is cast. An impurity structure portion in a surface of the slab is subjected to a face mill cutter so as to be cut by a depth in a range of from 3 to 10 mm. After the face mill cutting step, a heat holding step for holding a temperature in a range of from 480 to 540°C for a time in a range of from 6 to 12 hours is performed in a heat holding furnace in order to remove stress in the inside of the slab and make the structure uniform. Then, hot rolling is performed at a temperature in a range of from 480 to 540°C. After a thickness in a range of from 5 to 40 mm is obtained by the hot rolling, cold rolling is performed at room temperature to obtain a predetermined thickness. After annealing for making the structure uniform is performed so that the rolled structure, or the like, is homogenized, cold rolling is performed to a defined thickness to correct the plate to have good flatness. The thus produced aluminum support is used as a planographic printing plate support.

[0008] The electrolytic surface-roughening is, however, particularly easily affected by the aluminum support which is a subject. Therefore, when the aluminum support is produced by the steps of melting holding, casting, face mill cutting and heat holding, metal alloy components etc. in the surface layer of the aluminum support may scatter to bring a cause of lowering of yield of the planographic printing plate even in the case where not only heating and cooling are repeated but also a face mill cutting step for cutting the surface layer is provided.

[0009] On the contrary, the following method for producing a planographic printing plate support has been proposed as a method in which not only variation in the material of the aluminum support is reduced but also the yield of the electrolytic surface-roughening treatment is improved to thereby produce an excellent-quality good-yield planographic printing plate (U.S. Patent No. 5,078,805 corresponding to JP-A-3-79798). Namely, the method comprises the steps of continuously performing casting and hot rolling to form a thin-plate hot-rolled coil from molten aluminum, and performing cold rolling, heating and correction to roughen a surface of the aluminum support.

[0010] Further, the following methods have proposed. There are a method for defining the temperature difference at a leading end of a molten metal supply nozzle (U.S. Patent No. 5,462,614 corresponding to JP-A-6-262308), and a

method for defining the casting start temperature (JP-A-7-40017), when an aluminum support subjected to cold rolling, heating and correction is to be subjected to surface roughening treatment after a plate-like matter is continuously cast and rolled directly from molten aluminum by means of a pair of rolls.

[0011] Further, when a plate-like matter is continuously cast and rolled directly from molten aluminum by means of a pair of rollers, it is generally known that a liquid containing graphite is applied onto surfaces of the pair of cooling rollers (the pair of rollers) by a spray (Light Metal Age, October 1975, p19).

[0012] Further, with respect to the molten metal supply nozzle used for continuously casting and rolling a plate-like matter directly from molten aluminum by a pair of rollers, its schematic shape is described, for example, in Light Metal Age, October 1975, p6. With respect to its detailed shape, JP-B-52-23327 (hereinafter, JP-B means Examined Japanese Patent Publication), JP-A-2-290652, JP-A-1-215441, JP-A-62-248543, JP-A-61-1456, British Patent No. 2198976, U.S. Patent No. 4716956, Canadian Patent No. 619491, etc. are known as known patents.

[0013] Even in the case where the various proposed methods are used, stripe-like surface-quality defects may be generated continuously or intermittently in the aluminum plate in its rolling direction. That is, the flow of molten metal in the molten metal supply nozzle changes in accordance with the difference in the particle size distribution of a release agent applied onto the inner surface of the molten metal supply nozzle, so that the molten metal does not flow uniformly and stably. Accordingly, the flow-disturbed portions form stripe-like surface-quality defects. There arose a problem that the yield of production was lowered.

SUMMARY OF THE INVENTION

[0014] It is an object of the present invention to provide a method for producing a planographic printing plate support which is excellent in the yield of production owing to the suppression of the generation of stripe-like surface-quality defects appearing continuously or intermittently in an aluminum plate in its rolling direction.

[0015] In a method for producing a planographic printing plate support, aluminum is melted, molten aluminum is supplied a gap between a pair of cooling rollers from a molten metal supply nozzle, at least one of cold rolling and heating at least once to form an aluminum thin plate having a thickness in a range of from 0.1 mm to 0.5 mm, and the aluminum thin plate is corrected to form an aluminum support and roughen a surface of the aluminum support. The molten metal supply nozzle has an inner surface which is brought into contact with the molten metal and which is coated with aggregate particles having a particle size distribution with a median size in a range of from 5 μm to 20 μm and a mode size in a range of from 4 μm to 40 μm to thereby cast and roll plate-like aluminum continuously.

[0016] In a method according to the present invention, a release agent containing aggregate particles having a particle size distribution with a median size in a range of from 5 μm to 20 μm and a mode size in a range of from 4 μm to 40 μm is applied onto the inner surface of a molten metal supply nozzle. By the configuration in which molten aluminum is supplied from the molten metal supply nozzle to finally form an aluminum thin plate having a thickness in a range of from 0.1 mm to 0.5 mm, the flow of molten metal in the molten metal supply nozzle is uniform and stable owing to the function of the release agent containing aggregate particles to prevent stripe-like surface-quality defects. The particle size distribution with the mode size is preferably in the range of from 7 μm to 20 μm , and more preferably in the range of from 8 μm to 12 μm .

[0017] By the aforementioned configuration, stripe-like surface-quality defects appearing in the aluminum plate continuously or intermittently in its rolling direction are eliminated so that a planographic printing plate support good in surface quality can be produced with good yields.

[0018] Incidentally, in the present invention, boron nitride (BN), graphite, table, molybdenum disulfate, fluororesin, zirconium silicate or the like is used as the release agent, and water, organic solvent or the like is used as the aggregate contained in the release agent.

[0019] Further, a thin-plate continuous casting technique such as a Hunter method, a 3C method, or the like, has been put into practical use as the method for casting a plate-like matter directly from molten aluminum by using a twin roll to form a thin-plate coil.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] In the accompanying drawings:

Fig. 1 is a schematic view showing the steps of a method for producing a planographic printing plate support according to the present invention;

Fig. 2 is a schematic view of a cold rolling apparatus used in the present invention; and

Fig. 3 is a schematic view of a batch annealing apparatus used in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Detailed description of the present invention will be described as follows referring to the accompanying drawings.

[0022] In an embodiment according to the present invention, a method for producing an aluminum support according to the present invention will be described below more specifically with reference to the drawings. Fig. 1 is a schematic view showing the steps of the method for producing an aluminum support according to the present invention.

[0023] As shown in Fig. 1, a melting hold furnace 1 is tilted to thereby feed molten aluminum to a gutter 2. The liquid level of the gutter 2 is detected by a liquid level sensor 7 and a melting furnace tilting motor 9 is controlled through an amplifier 8 to thereby control the supply quantity of the molten metal to keep the liquid level of the gutter 2 constant. Further, a crystal particle refining wire 10 is supplied to the molten metal as occasion demands. In order to suppress the generation of oxide of the molten aluminum and remove an alkali metal harmful to quality, inert gas purging, fluxing, or the like, is performed suitably.

[0024] The molten metal is supplied to a gap between a pair of cooling rollers 4a and 4b from a molten metal supply nozzle 3 having an inner surface which is brought into contact with the molten metal and which is coated with a release agent containing aggregate particles having a particle size distribution with a median size in a range of from 5 μm to 20 μm and a mode size in a range of from 4 μm to 12 μm . When solidified and cooled, the molten metal is rolled to thereby produce a cast plate. For example, the cast plate ejected from the cooling rolls 4a and 4b can be wound up by a coiler 6 or can be sampled suitably by a cutter 5.

[0025] The thus obtained plate material is rolled into a defined thickness by a cold rolling apparatus 11 shown in Fig. 2. In this occasion, a heating step such as intermediate annealing, etc. may be performed and then the cold rolling apparatus 11 may be provided in order to make the crystal particle size uniform. Then, the plate material is corrected by a corrector to thereby give predetermined surface flatness, produce an aluminum support and roughen the surface of the aluminum support. Alternatively, correction may be included in the final cold rolling.

[0026] The method for roughening the surface of a planographic printing plate support according to the present invention is used variously for mechanical surface roughening, chemical surface roughening, electrochemical surface roughening, combination thereof, etc.

[0027] Examples of a mechanical graining method include a ball grain method, a wire grain method, a brush graining method, a liquid honing method, etc. As an electrochemical graining method, an AC electrolytic etching method is generally used, in which, as an electric current, an ordinary sinusoidal alternating current or a special alternating current such as a rectangular-wave current, or the like, is used. Further, etching with sodium hydroxide, or the like, may be performed as a treatment prior to the electrochemical graining.

[0028] Further, in the case of electrochemical surface roughening, the surface is preferably roughened by an alternating current in an aqueous solution mainly containing hydrochloric acid or nitric acid. Detail will be described below.

[0029] First, the aluminum support is alkali-etched. Examples of the preferred alkali agent are sodium hydroxide, potassium hydroxide, sodium metasilicate, sodium carbonate, sodium aluminate, sodium gluconate, etc. The concentration, temperature and time are preferably from a range of from 0.01 to 20 wt%, a range of from 20 to 90°C and a range of from 5 sec to 5 min, respectively. The preferred etching quantity is in a range of from 0.1 to 5 g/m^2 .

[0030] Particularly when the support contains a lot of impurities, the preferred etching quantity is in a range of from 0.01 to 1 g/m^2 (JP-A-1-237197). Succeedingly, desmutting may be performed as occasion demands, because alkali-insoluble components (smut) remains on the surface of the alkali-etched aluminum plate.

[0031] In any case, a stripe-like surface-quality defect appears as a result of the aforementioned etching with sodium hydroxide, or the like, when the stripe-like surface-quality defect is generated continuously or intermittently in the aluminum plate in its rolling direction.

[0032] The pre-treatment is as described above. Succeedingly, in the present invention, AC electrolytic etching is performed in an electrolytic solution mainly containing hydrochloric acid or nitric acid. The frequency of the AC electrolytic current is in a range of from 0.1 to 100 Hz, preferably in a range of from 0.1 to 1.0 or from 10 to 60 Hz. The liquid concentration is in a range of from 3 to 150 g/l, preferably in a range of from 5 to 50 g/l. The quantity of aluminum dissolved in a bath is preferably not larger than 50 g/l, more preferably in a range of from 2 to 20 g/l. Additives may be mixed if necessary, but if so, liquid concentration, control, or the like, becomes difficult in the case of mass production.

[0033] Further, the current density is preferably in a range of from 5 to 100 A/dm^2 , more preferably in a range of from 10 to 80 A/dm^2 . Further, the electric source waveform is selected suitably in accordance with the required quality and the components of the aluminum support used. A special alternating waveform described in JP-B-56-19280 and JP-B-55-19191 is used more preferably. The waveform and liquid condition are selected suitably in accordance with electrical quantity, required quality, components of the used aluminum support, etc.

[0034] The electrolytically surface-roughened aluminum is then immersed in an alkali solution as a part of a smutting treatment so that smut is dissolved. Although various alkali agents such as sodium hydroxide, etc. are used, the immersion is preferably performed in a pH value not smaller than 10, at a temperature of 25 to 60°C in an extremely short

immersion time of 1 to 10 sec.

[0035] The aluminum is then immersed in a solution mainly containing sulfuric acid. The preferred liquid condition for sulfuric acid is a concentration in a range of from 50 to 400 g/l greatly lower than the conventional concentration and a temperature in a range of from 25 to 65°C. If the sulfuric acid concentration is not lower than 400 g/l or if the temperature is not lower than 65°C, not only corrosion of a treating tank, or the like, increases but also electrochemically surface-roughened particles are collapsed in an aluminum alloy containing 0.3 % or more of manganese. Further, if etching is performed so that the quantity of the dissolved aluminum ground is not smaller than 0.2 g/m², printing endurance is lowered. Accordingly, the quantity of the dissolved aluminum ground is preferably not larger than 0.2 g/m².

[0036] An anodic oxide film is formed on the surface preferably in a range of from 0.1 to 10 g/m², more preferably from 0.3 to 5 g/m².

[0037] The condition for anodic oxidation cannot be determined sweepingly because the condition change variously in accordance with the electrolytic solution used. Generally, the preferred condition is an electrolyte concentration in a range of from 1 to 80 % by weight, a liquid temperature in a range of from 5 to 70°C, a current density in a range of from 0.5 to 60 A/dm², a voltage in a range of from 1 to 100 V and an electrolysis time of 1 sec to 5 min.

[0038] The thus obtained grained aluminum plate having an anodic oxide film itself is stable and excellent in hydrophilic nature. Accordingly, a light-sensitive coating film can be provided on the aluminum plate directly or a surface treatment can be further applied to the aluminum plate, if necessary.

[0039] For example, a silicate layer of alkali-metal silicate or an undercoating layer of a hydrophilic high-molecular compound as described above can be provided. The coating quantity of the undercoating layer is preferably in a range of from 5 to 150 mg/m².

[0040] A light-sensitive coating film is then provided on the aluminum support treated in the aforementioned manner. After image exposure, development and plate making, the plate is set in a printing machine to start printing.

EXAMPLES

[0041] Basic steps in the examples according to the present invention in a casting step portion of the method for producing a planographic printing plate aluminum support will be described below in accordance with the steps of the method for producing an aluminum support in Fig. 1. First, the temperature of molten aluminum is kept at 790°C in the melting hold furnace 1. When the molten metal is poured, an alloy wire of Al-Ti(5%)-B(1%) which is the crystal particle refining wire 10 is supplied as a particle refining agent and dissolved in the molten metal.

[0042] The molten metal is then supplied to a gap between the pair of cooling rollers 4a and 4b from the molten metal supply nozzle 3 having an inner surface which is brought into contact with the molten metal and which is coated with a release agent containing aggregate particles. While being solidified and cooled, the molten metal is continuously cast and rolled to form a plate having a thickness of 7.0 mm and a width of 200 mm. The plate is wound up by the coiler 6. Further, the plate is rolled into a thickness of 1.5 mm by the cold rolling apparatus 11 shown in Fig. 2. The plate is then heated at 480°C for 10 hours by a batch annealing apparatus 12 shown in Fig. 3. Finally, the plate is rolled again into a thickness of 0.24 mm by the cold rolling apparatus 11.

[0043] With respect to the state of the release agent containing aggregate particles and applied onto the inner surface of the molten metal supply nozzle 3 brought into contact with the molten metal, the following experiments were executed.

Examples 1 - 8

[0044] A release agent exhibiting a particle size distribution with a median size and a mode size described in Table 1 was applied onto the molten metal supply nozzle 3.

Comparative Example 1 - 5

[0045] A release agent exhibiting a particle size distribution with a median size and a mode size described in Table 1 was applied onto the molten metal supply nozzle 3.

Table 1

	Median Diameter (μm)	Mode Diameter (μm)
Example 1	6.5	10.0
Example 2	5.5	8.0

Table 1 (continued)

	Median Diameter (μm)	Mode Diameter (μm)
Example 3	5.5	7.0
Example 4	5.0	4.2
Example 5	15.0	20.0
Example 6	10.0	12.0
Example 7	16.0	22.0
Example 8	19.5	39.0
Comparative Example 1	1.5	1.5
Comparative Example 2	21.0	20.0
Comparative Example 3	24.0	10.0
Comparative Example 4	30.0	43.3
Comparative Example 5	3.0	3.4

Table 2

	External Appearance after etching	EPMA ANALYSIS RESULTS
Example 1	Excellent	No segregation appeared
Example 2	Excellent	No segregation appeared
Example 3	Good	Weak segregation appeared in the Fe stripe portion
Example 4	Acceptable	Weak segregation appeared in the Fe/Si stripe portion
Example 5	Good	Weak segregation appeared in the Fe stripe portion
Example 6	Excellent	No segregation appeared
Example 7	Practical	Weakest segregation appeared in the Fe/Si stripe portion
Example 8	Acceptable	Weak segregation appeared in the Fe/Si stripe portion
Comparative Example 1	Bad	Strong segregation appeared in the Fe/Si stripe portion
Comparative Example 2	Bad	Strong segregation appeared in the Fe/Si stripe portion
Comparative Example 3	Bad	Strong segregation appeared in the Fe/Si stripe portion
Comparative Example 4	Bad	Strong segregation appeared in the Fe/Si stripe portion
Comparative Example 5	Bad	Strong segregation appeared in the Fe/Si stripe portion

[0046] Each of the samples prepared as described above was etched with an aqueous solution of 15 % sodium hydroxide at a liquid temperature of 60°C so that the quantity of etching was 5 g/m². The external appearance concerning the situation of generation of crystal stripes was checked. For samples in which stripes were generated, components of the crystal stripe portion were analyzed by EPMA to confirm whether segregation of Fe and Si as a characteristic of the stripe portion exists or not. The results are as shown in Table 2.

[0047] As described above, in the method for producing a planographic printing plate support according to the present invention, stripe-like surface-quality defects (crystal stripes) generated in an aluminum plate continuously or intermittently in its rolling direction are eliminated so that a planographic printing plate aluminum support which is good in surface quality can be manufactured.

Claims

1. A method for producing a planographic printing plate support comprising the steps of:

5 melting aluminum;
 supplying molten aluminum to a gap between a pair of cooling rollers from a molten metal supply nozzle having an inner surface which is brought into contact with the molten metal and which is coated with aggregate particles having a particle size distribution with a median size in a range of from 5 μm to 20 μm and a mode size in a range of from 4 μm to 40 μm to thereby cast and roll plate-like aluminum continuously;
 10 performing at least one of cold rolling and heating at least once to form an aluminum thin plate having a thickness in a range of from 0.1 mm to 0.5 mm; and
 correcting the aluminum thin plate to form an aluminum support and roughen a surface of said aluminum support.

15 2. A method as claimed in claim 1, wherein said particle size distribution with the mode size is in a range of from 7 μm to 20 μm .

3. A method as claimed in claim 1, wherein said particle size distribution with the mode size is in a range of from 8 μm to 12 μm .

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FIG. 1

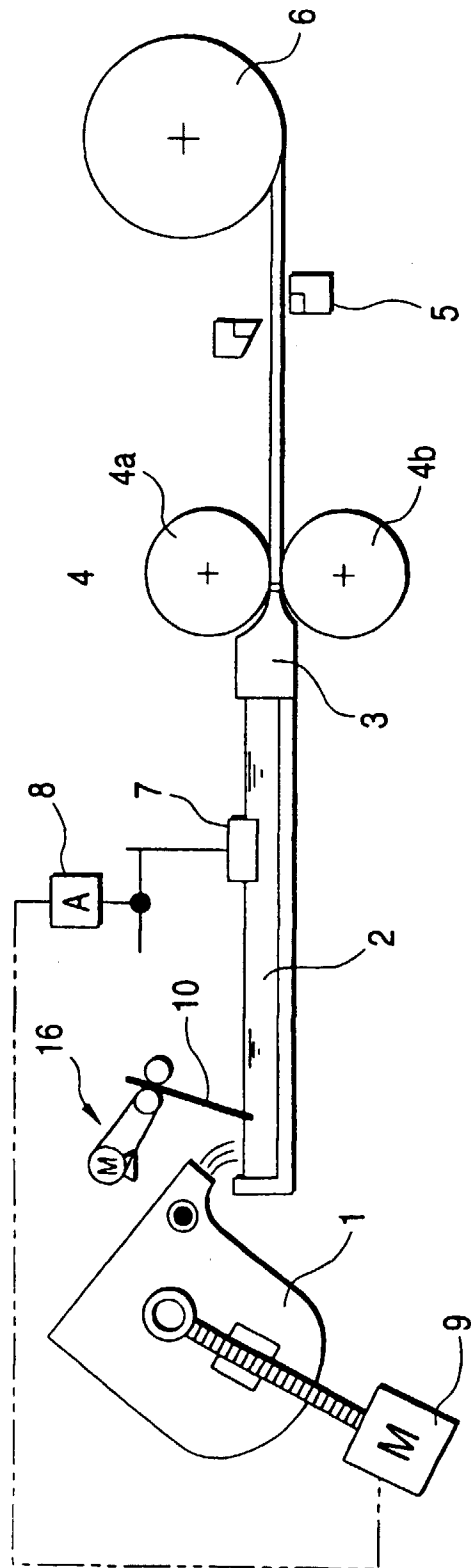


FIG. 2

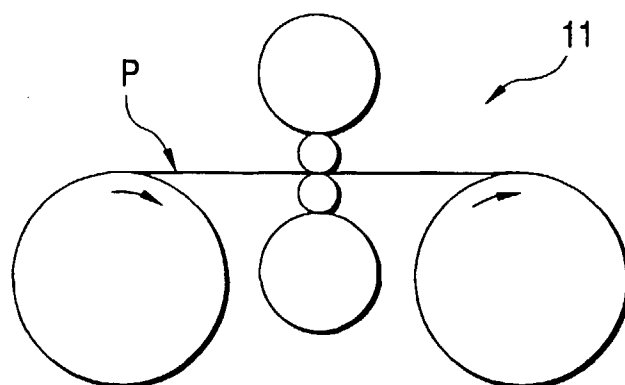
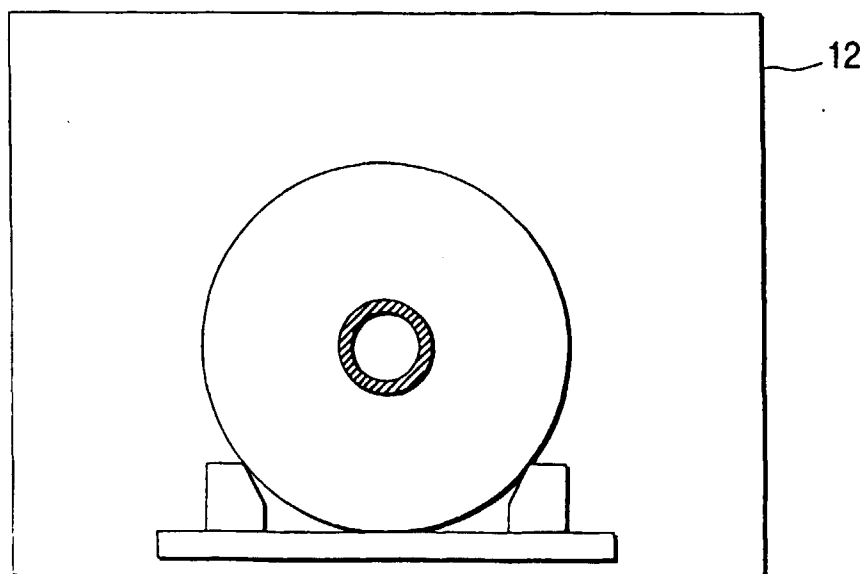


FIG. 3





European Patent
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Application Number
EP 99 10 0102

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The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 21 April 1999	Examiner Sutor, W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EUROPEAN SEARCH REPORT

Application Number
EP 99 10 0102

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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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

EP 99 10 0102

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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