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(72) Inventor: **CASTENIER, Adrien**

Outremont, Quebec H2V 2Z2 (CA)

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(74) Representative:

**Koepe, Gerd L., Dipl.-Chem.
Blumbach, Kramer & Partner GbR,
Patentanwälte,
Radeckestrasse 43
81245 München (DE)**

(71) Applicant:

**TOYO INK MANUFACTURING CO., LTD.
Chuo-ku, Tokyo 173 (JP)**

(54) **ELECTRIC COAGULATION PRINTING METHOD AND APPARATUS**

(57) An electric coagulation printing method comprising the step (a) of forming a plurality of dots of colored coagulation ink, which represent a desired image, on an active surface of an anode by electric coagulation of the electric coagulation printing ink, and the step (b) of bringing a substrate into contact with the dots of colored coagulation ink so as to transfer the same ink from the active surface of the anode to the substrate, whereby the image is printed on the substrate, characterized in that the step (a) is carried out while the active surface of the anode and ink is maintained at a temperature of about 35° - 60°C. An apparatus for implementing this method is also disclosed.

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Description

TECHNICAL FIELD

[0001] The present invention pertains to improvements in the field of electrocoagulation printing. More particularly, the invention relates to a method of increasing coagulation efficiency and improving optical density of the printed matter during electrocoagulation printing.

BACKGROUND ART

PRIOR ART

[0002] In US Patent No. 4,895,629 of January 23, 1990, the inventor has described a high-speed electrocoagulation printing method and apparatus in which use is made of a positive electrode in the form of a revolving cylinder having a passivated surface onto which dots of colored, coagulated ink representative of an image are produced. These dots of colored, coagulated ink are thereafter contacted with a substrate such as paper to cause transfer of the colored, coagulated ink onto the substrate and thereby imprint the substrate with the image. As explained in this patent, the positive electrode is coated with an oily substance prior to electrical energization of the negative electrodes in order to weaken the adherence of the dots of coagulated ink to the positive electrode and also to prevent an uncontrolled corrosion of the positive electrode. In addition, gas generated as a result of electrical energization of the negative electrodes is consumed by reaction with an olefinic substance so that there is no gas accumulation between the negative and positive electrodes.

[0003] The electrocoagulation printing ink which is injected into the gap defined between the positive and negative electrodes consists essentially of a solution or a dispersion containing an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent. Where the coloring agent used is a pigment, a dispersing agent is added for uniformly dispersing the pigment into the ink. After coagulation of the ink, any remaining non-coagulated ink is removed from the surface of the positive electrode, for example, by scraping the surface with a soft rubber squeegee, so as to fully uncover the colored, coagulated ink which is thereafter transferred onto the substrate. The surface of the positive electrode is thereafter cleaned by means of a plurality of rotating brushes and a cleaning liquid to remove any residual coagulated ink and oily substance adhered to the surface of the positive electrode.

[0004] When a polychromatic image is desired, the negative and positive electrodes, the oily substance coating device, ink injector, rubber squeegee and positive electrode cleaning device are arranged to define a printing unit and several printing units each using a coloring agent of different color are disposed in tandem relation to produce several differently colored images of

coagulated ink which are transferred at respective transfer stations onto the substrate in superimposed relation to provide the desired polychromatic image. Alternatively, the printing units can be arranged around a single roller adapted to bring the substrate into contact with the dots of colored, coagulated ink produced by each printing unit, and the substrate which is in the form of a continuous web is partially wrapped around the roller and passed through the respective transfer stations for being imprinted with the differently colored images in superimposed relation.

PROBLEMS TO BE SOLVED

[0005] The electrocoagulation printing method described in the aforementioned US Patent No. 4,895,629 is carried out at room temperature which is generally about 25 - 30°C. The inventor has observed that the maximum optical density of the dots of colored, coagulated ink formed on the positive electrode active surface and then printed on the substrate, that could be reached with an ink having a temperature of 30°C and with a voltage of 55 volts applied for 4 microseconds between the negative and positive electrodes, was 1.60. By increasing the voltage to 60 volts under the same conditions, there was no valuable increase in the optical density of the coagulated ink, but rather an undesirable gas generation between the electrodes. If the concentration of the electrolyte in the ink was reduced to control the gas generation, a reduction in the optical density of the coagulated ink was observed.

[0006] Also the inventor has observed that most of the papers used as substrates for electrocoagulation printing had to be humidified with a mist of water in order to prevent a part of the dots of colored, coagulated ink from remaining on the positive electrode when being transferred from the positive electrode active surface onto the paper. Without paper humidification, only about 60 - 70% of the colored, coagulated ink were transferred onto dry paper, a substantial amount of the coagulated ink remaining on the positive electrode surface.

[0007] When using a water absorbent paper, a slight humidification of the paper caused up to about 90% of the colored, coagulated ink to be transferred. However, the humidified paper suffered a reduction in mechanical strength. Humidification of newspaper which is a thin water absorbent paper having a thickness of about 60 - 70 µm was also impossible since newspaper cannot sustain humidification without tearing.

DISCLOSURE OF INVENTION

[0008] It therefore is an object of the present invention to overcome the above drawbacks and to provide a method and an apparatus for increasing the efficiency of coagulation and improving the optical density of the printed matter.

[0009] In accordance with the present invention, there

is provided an improved electrocoagulation printing method comprising the steps of:

a) providing a positive electrode having an active surface, and forming a plurality of dots of colored, coagulated ink representative of a desired image on the positive electrode active surface by electrocoagulation of an electrolytically coagulable printing ink; and

b) bringing a substrate into contact with the dots of colored, coagulated ink to transfer the colored, coagulated ink onto the substrate from the positive electrode active surface, to thereby print the image onto the substrate; wherein

the step (a) is carried out while maintaining the positive electrode active surface and the ink at a temperature of from about 35 °C to about 60 °C.

[0010] Moreover, there is provided an electrocoagulation printing apparatus for carrying out the improved method of this invention, comprising:

a positive electrode having an active surface; means for supplying an electrolytically coagulable printing ink to the positive electrode;

means for forming a plurality of dots of colored, coagulated ink representative of a desired image on the positive electrode active surface by electrocoagulation of the ink;

means for bringing a substrate into contact with dots of the colored, coagulated ink to cause a transfer of the colored, coagulated ink onto the substrate from the positive electrode active surface, to thereby print the image onto the substrate; and

heating means for maintaining the temperature of the positive electrode active surface and the ink at from about 35 °C to about 60 °C.

[0011] This improved electrocoagulation printing method is further described in detail. That is, in accordance with the present invention, there is provided an improved electrocoagulation printing method comprising the steps of:

a) providing a positive electrode having a continuous passivated surface, moving at substantially constant speed along a predetermined path, and forming on the positive electrode active surface a plurality of dots of colored, coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable polymer present in an electrocoagulation printing ink comprising a solution or a dispersion containing the electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent; and

b) bringing a substrate into contact with the dots of colored, coagulated ink to cause a transfer of the colored, coagulated ink from the positive electrode

active surface onto the substrate and thereby imprint the substrate with the image; wherein the step (a) is carried out while maintaining the positive electrode active surface and the ink at a temperature of from about 35°C to about 60°C.

[0012] Maintaining the positive electrode active surface and the ink at the temperature of from about 35°C to about 60°C causes an increase in the electric conductivity of the ink and a release of metal ions from the positive electrode active surface into the ink in step (a). Thereby the metal ions are released in a quantity sufficient to increase optical density of the coagulated ink, and a coagulation efficiency in step (a) is increased.

[0013] A break down of passive oxide layer occurs easily in the presence of electrolyte anions, such as Cl⁻, Br⁻ and I⁻, there being a gradual oxygen displacement from the passive oxide layer by the halide anions and a displacement of absorbed oxygen from the metal surface by the halide anions. The velocity of passive oxide layer breakdown, once started, increases explosively by an electrical energizing. There is thus formation of a soluble metal halide at the metal surface. In other words, a local dissolution of the passive oxide layer at the breakdown sites, which releases metal ions into the electrolyte solution. Where a positive electrode made of stainless steel or aluminum is utilized in inventor's electrocoagulation printing method, dissolution of the passive oxide layer on such a positive electrode generates Fe³⁺ or Al³⁺ ions. These trivalent ions then initiate coagulation of the ink.

[0014] It has surprisingly been found, according to the invention, that by increasing the temperature of the positive electrode active surface as well as the temperature of ink to within the range of from about 35°C to about 60°C, preferably to about 50°C, and more preferably to about 45°C, not only is there an increase in the conductivity of the ink which assists electrocoagulation, but there is also an increase in the rate of local dissolution of the passive oxide layer on the positive electrode, which causes a greater quantity of metal ions to be released into the ink. If the temperature of the positive electrode active surface is below 35°C, the quantity of metal ions released into the ink is insufficient for obtaining the desired increase in the optical density of the coagulated ink. At a temperature above 60°C, problems such as condensation of water vapor on the equipment are encountered.

[0015] When operating at the temperature of about 40°C with an ink having a reduced electrolyte concentration and with a voltage of 60 volts, the method according to the invention enables one to obtain dots of colored, coagulated ink having an optical density of 1.70.

BRIEF DESCRIPTION OF DRAWINGS

[0016]

Figure 1 shows a schematic illustration of the electrocoagulation printing apparatus (1) embodying the present invention.

Figure 2 shows a schematic illustration of an embodiment of the heating unit for the positive cylindrical electrode. The positive cylindrical electrode is heated and maintained at the temperature of from about 35°C to about 60°C by carrying heated liquid or gas through a vent located on the central longitudinal axis of the positive cylindrical electrode.

Figure 3 shows a schematic illustration of another embodiment of the heating unit for heating the electrocoagulation printing ink before supplying it onto the positive electrode active surface. The ink is heated and maintained at the temperature of from about 35°C to about 60°C when passing through this apparatus.

Figure 4 shows a schematic illustration of further embodiment of the heating unit for heating the positive electrode active surface from the outside.

Figure 5 shows a schematic illustration of further embodiment of the heating unit for heating the positive electrode by cleaning liquid. That is, the positive cylindrical electrode is heated by heating the cleaning liquid and directing jets thereof against the positive electrode.

Figure 6 shows a cross sectional schematic illustration of an embodiment of cleaning unit for cleaning the positive electrode active surface to remove therefrom any remaining coagulated ink, comprising a jet means for directing jets of the cleaning liquid against the positive electrode active surface.

Figure 7 is a graph showing the variation of the ink conductivity as a function of the temperature thereof. As shown in this figure, the conductivity of the ink increases with an increase in the temperature thereof.

Figure 8 is a graph showing an example of the connection between the temperature of the positive electrode active surface as well as of the ink and the optical density, indicating the increase of the optical density by the increase in the temperature up to 35°C and above.

BEST MODE FOR CARRYING OUT THE INVENTION

[0017] Where a polychromatic image is desired, steps (a) and (b) of the above electrocoagulation printing method are repeated several times to define a corresponding number of printing stages arranged at predetermined locations along the aforesaid path and each using a coloring agent of different color, and to thereby produce several differently colored images of coagu-

lated ink which are transferred at the respective transfer positions onto the substrate in superimposed relation to provide a polychromatic image.

[0018] The positive electrode used can be in the form of a moving endless belt as described in US Patent No. 4,661,222, or in the form of a revolving cylinder as described in US Patent No. 4,895,629 or in US Patent No. 5,538,601. In the later case, the printing stages are arranged around the positive cylindrical electrode. Preferably, the positive electrode active surface and the ink are maintained at a temperature of about 35 - 60°C by heating the positive electrode active surface and applying the ink on the heated electrode surface to cause a transfer of heat therefrom to the ink.

[0019] When use is made of a positive electrode of cylindrical configuration rotating at substantially constant speed about its central longitudinal axis, step (a) of the above electrocoagulation printing method is carried out by:

- i) providing a plurality of negative electrodes electrically insulated from one another and arranged in rectilinear alignment to define a series of corresponding negative electrode active surfaces disposed in a plane parallel to the longitudinal axis of the positive electrode and spaced from the positive electrode active surface by a constant predetermined gap, the negative electrodes being spaced from one another by a distance at least equal to the electrode gap;
- ii) coating the positive electrode active surface with an oily substance to form micro-droplets thereof on the surface;
- iii) filling the electrode gap with the aforesaid electrocoagulation printing ink;
- iv) electrically energizing selected ones of the negative electrodes to cause point-by-point selective coagulation and adherence of the ink onto the oily substance-coated positive electrode active surface opposite the electrode active surfaces of the energized negative electrodes while the positive electrode is rotating, thereby forming the dots of colored, coagulated ink; and
- v) removing any remaining non-coagulated ink from the positive electrode active surface.

[0020] As explained in US Patent No. 4,895,629, spacing of the negative electrodes from one another by a distance which is equal to or greater than the electrode gap prevents the negative electrodes from undergoing edge corrosion. On the other hand, coating of the positive electrode with an oily substance prior to electrical energization of the negative electrodes weakens the adherence of the dots of coagulated ink to the positive electrode and also prevents an uncontrolled corrosion of the positive electrode. In addition, in a case of the oily substance being an olefinic substance, gas generated as a result of electrolysis upon energizing the negative

electrodes is consumed by reaction with the olefinic substance so that there is no gas accumulation between the negative and positive electrodes.

[0021] Examples of suitable metals from which the positive and negative electrodes can be made are stainless steel, platinum, chromium, nickel, tin and aluminum. The positive electrode is preferably made of stainless steel, aluminum or tin so that upon electrical energization of the negative electrodes, dissolution of the passive oxide layer on such an electrode generates trivalent ions which then initiate coagulation of the ink.

[0022] The gap which is defined between the positive and negative electrodes can range from about 50 μm to about 100 μm , the smaller the electrode gap the sharper are the dots of coagulated ink produced. Where the electrode gap is of the order of 50 μm , the negative electrodes are the preferably spaced from one another by a distance of about 75 μm .

[0023] Olefinic substances are preferably used as an oily substance for being used to coat the surface of the positive electrode in step (a)(ii). Examples of the suitable olefinic substances include unsaturated fatty acids such as arachidonic acid, linoleic acid, linolenic acid, oleic acid and palmitoleic acid and unsaturated vegetable oils such as corn oil, linseed oil, olive oil, peanut oil, soybean oil and sunflower oil. The olefinic substance can be applied onto the positive electrode active surface in the form of an oily dispersion containing the metal oxide as dispersed phase. Examples of suitable metal oxides include aluminum oxide, ceric oxide, chromium oxide, cupric oxide, magnesium oxide, manganese oxide, titanium dioxide and zinc oxide. Depending on the type of metal oxide used, the amount of metal oxide may range from about 15 to about 40% by weight, based on the total weight of the dispersion. A particularly preferred dispersion contains about 75 wt.% of oleic acid or linoleic acid and about 25 wt.% of chromium oxide. Operating at a temperature of about 35 - 60°C enables one to lower the concentration of metal oxide in the oily dispersion and thus to reduce wear of the positive electrode active surface.

[0024] The oily substance is advantageously applied onto the positive electrode active surface by providing a distribution roller extending parallel to the positive cylindrical electrode and having a peripheral coating comprising an oxide ceramic material, applying the oily substance onto the ceramic coating to form on a surface thereof a film of the oily substance uniformly covering the surface of the ceramic coating, the film of oily substance breaking down into micro-droplets having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating onto the positive electrode active surface. As explained in US Patent No. 5,449,392 of September 12, 1995, the use of a distribution roller having a ceramic coating comprising an oxide ceramic material enables one to form on a surface of such a coating a film of the oily substance which uniformly covers the surface of the ceramic coating and

thereafter breaks down into micro-droplets having substantially uniform size and distribution. The micro-droplets formed on the surface of the ceramic coating and transferred onto the positive electrode active surface generally have a size ranging from about 1 to about 5 μm .

[0025] A particularly preferred oxide ceramic material forming the aforesaid ceramic coating comprises a fused mixture of alumina and titania. Such a mixture may comprise about 60 to about 90 weight % of alumina and about 10 to about 40 weight % of titania.

[0026] According to a preferred embodiment of the invention, the oily substance is applied onto the ceramic coating by disposing an applicator roller parallel to the distribution roller and in pressure contact engagement therewith to form a first nip, and rotating the applicator roller and the distribution roller in register while feeding the oily substance into the first nip, whereby the oily substance upon passing through the first nip forms a film uniformly covering the surface of the ceramic coating. The micro-droplets are advantageously transferred from the distribution roller to the positive electrode by disposing a transfer roller parallel to the distribution roller and in contact engagement therewith to form a second nip, positioning the transfer roller in pressure contact engagement with the positive electrode to form a third nip, and rotating the transfer roller and the positive electrode in register for transferring the micro-droplets from the distribution roller to the transfer roller at the second nip and thereafter transferring the micro-droplets from the transfer roller to the positive electrode at the third nip. Such an arrangement of rollers is described in the aforementioned US Patent No. 5,449,392.

[0027] Preferably, the applicator roller and the transfer roller are each provided with a peripheral covering of a resilient material which is resistant to attack by the oily substance, such as a synthetic rubber material. For example, use can be made of a polyurethane having a Shore A hardness of from about 50 to about 70 in the case of the applicator roller, or a Shore A hardness of from about 60 to about 80 in the case of the transfer roller.

[0028] In some instances, depending on the type of oily substance used, inventor has noted that the film of oily substance only partially breaks down on the surface of the ceramic coating into the desired micro-droplets. Thus, in order to ensure that the film of oily substance substantially completely breaks on the ceramic coating into micro-droplets of oily substance having substantially uniform size and distribution step (a)(ii) of the electrocoagulation printing method of the invention is preferably carried out by providing first and second distribution rollers extending parallel to the positive cylindrical electrode and each having a peripheral coating comprising an oxide ceramic material, applying the oily substance onto the ceramic coating of the first distribution roller to form on a surface thereof a film of the oily

substance uniformly covering the surface of the ceramic coating, the film of oily substance at least partially breaking down into micro-droplets having substantially uniform size and distribution, transferring the at least partially broken film from the first distribution roller to the second distribution roller so as to cause the film to substantially completely break on the ceramic coating of the second distribution roller into the desired micro-droplets having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating of the second distribution roller onto the positive electrode active surface. Preferably, the ceramic coatings of the first distribution roller and the second distribution roller comprise the same oxide ceramic material. Such an arrangement of rollers is described in US Patent No. 5,538,601 of July 23, 1996.

[0029] According to a preferred embodiment, the oily substance is applied onto the ceramic coating of the first distribution roller by disposing an applicator roller parallel to the first distribution roller and in pressure contact engagement therewith to form a first nip, and rotating the applicator roller and the first distribution roller in register while feeding the oily substance into the first nip, whereby the oily substance upon passing through the first nip forms a film uniformly covering the surface of the ceramic coating.

[0030] According to another preferred embodiment, the at least partially broken film of oily substance is transferred from the first distribution roller to the second distribution roller and the micro-droplets are transferred from the second distribution roller to the positive electrode by disposing a first transfer roller between the first distribution roller and the second distribution roller in parallel relation thereto, positioning the first transfer roller in pressure contact engagement with the first distribution roller to form a second nip and in contact engagement with the second distribution roller to form a third nip, rotating the first distribution roller and the first transfer roller in register for transferring the at least partially broken film from the first distribution roller to the first transfer roller at the second nip, disposing a second transfer roller parallel to the second distribution roller and in pressure contact engagement therewith to form a fourth nip, positioning the second transfer roller in pressure contact engagement with the positive electrode to form a fifth nip, and rotating the second distribution roller, the second transfer roller and the positive electrode in register for transferring the at least partially broken film from the first transfer roller to the second distribution roller at the third nip, then transferring the micro-droplets from the second distribution roller to the second transfer roller at the fourth nip and thereafter transferring the micro-droplets from the second transfer roller to the positive electrode at the fifth nip. Such an arrangement of rollers is also described in the aforementioned US Patent No. 5,538,601. Preferably, the applicator roller, first transfer roller and second transfer roller are each provided with a peripheral covering of a

resilient material which is resistant to attack by the oily substance.

[0031] The oily substance-coated positive active surface is preferably polished to increase the adherence of the micro-droplets onto the positive electrode active surface, prior to step (a)(iii). For example, use can be made of a rotating brush provided with a plurality of radially extending bristles made of horsehair and having extremities contacting the surface of the positive electrode. The friction caused by the bristles contacting the surface upon rotation of the brush has been found to increase the adherence of the micro-droplets onto the positive electrode active surface.

[0032] Step (a)(iii) of the above electrocoagulation printing method is advantageously carried out by continuously injecting the ink onto the positive electrode active surface from a ink injection means disposed adjacent the electrode gap and allowing the ink to flow along the positive electrode active surface, the ink being thus carried by the positive electrode upon rotation thereof to the electrode gap to fill same. Preferably, excess ink flowing off the positive electrode active surface is collected and the collected ink is recirculated back to the ink injection means.

[0033] The electrocoagulation printing ink being electrolytically coagulable, contains at least an electrolytically coagulable polymer, a coloring agent, a liquid medium and a soluble electrolyte.

[0034] The polymer generally used has a weight-average molecular weight between about 10,000 and about 1,000,000, preferably between 100,000 and 600,000. Examples of the polymer include natural polymers such as albumin, gelatin, casein and agar, and synthetic polymers such as polyacrylic acid and polyacrylamide. A particularly preferred polymer is an anionic copolymer of acrylamide and acrylic acid having a molecular weight of about 250,000 and sold by Cyanamid Inc. under the trade name ACCOSTRENGTH 86. The polymer is preferably used in an amount of about 6.5 to about 12% by weight, and more preferably in an amount of about 7 to about 10% by weight, based on the total weight of the ink.

[0035] Preferred electrolytes include alkali metal halides, such as lithium chloride, sodium chloride and potassium chloride, and also alkaline earth metal halides, such as calcium chloride. Potassium chloride is particularly preferred. The electrolyte is preferably used in an amount of about 4.5 to about 10% by weight, based on the total weight of the ink. Incidentally, less electrolyte may be required at a temperature of about 35 - 60°C than at room temperature in order to counterbalance the increase in the ink conductivity at 35 - 60°C. The coloring agent can be a dye or a pigment. Examples of suitable dyes include indigo dye, azo dye, anthraquinone dye, fluoran dye, dioxazine dye, oxazine dye, phthalocyanine dye, etc.

[0036] Examples of suitable pigments include organic pigments such as azo pigment, phthalocyanine pig-

ment, anthraquinone pigment, dioxazine pigment, thio-indigo pigment, perynone pigment, perylene pigment, isoindolinone pigment and azomethine pigment, and inorganic pigments such as carbon black.

[0037] A dispersing agent is added for uniformly dispersing the pigment into the ink. Preferred dispersing agents include the anionic dispersing agent; a metal salt of naphthalenesulfonic acid-formaldehyde condensation product. The pigment is preferably used in an amount of about 6.5 to about 12% by weight, and the dispersing agent in an amount of about 0.4 to about 6% by weight, based on the total weight of the ink.

[0038] Water is preferably used as the liquid medium for dissolving or dispersing the aforesaid polymer, coloring agent and electrolyte to provide the desired ink.

[0039] After coagulation of the ink, any remaining non-coagulated ink is removed from the positive electrode active surface, for example, by scraping the surface with a soft rubber squeegee, so as to fully uncover the colored, coagulated ink. Preferably, the non-coagulated ink thus removed is collected and mixed with the collected ink, and the collected non-coagulated ink in admixture with the collected ink is recirculated back to the aforesaid ink injection means.

[0040] The optical density of the dots of colored, coagulated ink may be varied by varying the voltage and/or pulse duration of the pulse-modulated signals applied to the negative electrodes.

[0041] According to a preferred embodiment, the substrate is in the form of a continuous web. Step (b) is preferably carried out by providing at each transfer position a pressure roller extending parallel to the positive cylindrical electrode and in pressure contact engagement therewith to form a nip and permit the pressure roller to be driven by the positive electrode upon rotation thereof, and guiding the web so as to pass through the nip.

[0042] Preferably, the pressure roller is provided with a peripheral covering a synthetic rubber material such as a polyurethane having a Shore A hardness of about 95. A polyurethane covering with such a hardness has been found to further improve transfer of the colored, coagulated ink from the positive electrode active surface onto the substrate. The pressure exerted between the positive electrode and the pressure roller preferably ranges from about 50 to about 100 kg/cm².

[0043] After step (b), the positive electrode active surface is generally cleaned to remove therefrom any remaining coagulated ink. According to a preferred embodiment, the positive electrode is rotatable in a predetermined direction and any remaining coagulated ink is removed from the positive electrode active surface by providing an elongated rotatable brush extending parallel to the longitudinal axis of the positive electrode, the brush being provided with a plurality of radially extending bristles made of horsehair and having extremities contacting the positive electrode active surface, rotating the brush in a direction opposite to the direction of rota-

tion of the positive electrode so as to cause the bristles to frictionally engage the positive electrode active surface, and directing jets of cleaning liquid under pressure against the positive electrode active surface, from either side of the brush. In such an embodiment, the positive electrode active surface and the ink are preferably maintained at a temperature of about 35 - 60°C by heating the cleaning liquid to thereby heat the positive electrode active surface upon contacting same and applying the ink on the heated electrode surface to cause a transfer of heat therefrom to the ink.

[0044] Next, an apparatus used for electrocoagulation printing method improved by the present invention will be described based on the accompanying drawings.

[0045] Fig.1 shows an outline of an electrocoagulation printing apparatus 1 improved by the present invention. The electrocoagulation printing apparatus 1 includes a base plate 5 supported by a plurality of legs 3. On the base plate 5, a plurality of frames 7 are uprightly extended in a vertical direction. A pair of vertical plates 9 are provided on upper portion of the frames 7, and a cylindrical positive electrode 11 which is rotatable by a drive motor (not shown) is sandwiched between both the vertical plates 9. The positive electrode 11 is extended perpendicularly with respect to a paper surface of Fig.1, and includes a positive electrode active surface.

[0046] The electrocoagulation printing apparatus 1 comprises: a coating means 13 for coating the positive electrode active surface along the positive electrode 11 with an oily substance to form micro-droplets of the oily substance on the positive electrode active surface; an ink injection means 15 for supplying electrocoagulation printing ink to the positive electrode; a printing head 19 having negative electrodes 17 for forming, on the positive electrode active surface, a plurality of dots of colored, coagulated ink representing a desired image; and removing means 21 such as a squeegee for removing non-coagulated ink from the positive electrode active surface. A pressure roller 23 is further provided as means for bringing a substrate W and the plurality of dots of colored, coagulated ink representing the desired image on the obtained positive electrode active surface into contact with each other to transfer the colored, coagulated ink onto the substrate from the positive electrode active surface, thereby print the image onto the substrate.

[0047] Cleaning means 25 is provided below the positive electrode 11 for cleaning the positive electrode active surface to remove all the remaining coagulated ink from the positive electrode active surface.

[0048] With such a structure, the micro-droplets of the oily substance is applied, by the coating means 13, onto the active surface of the rotating positive electrode 11 and then, the ink is supplied between the negative electrodes 17 and the positive electrode 11 of the printing head 19 by the ink injection means 15. The supplied ink is coagulated by applying voltage between the elec-

trodes to form dots of coagulated ink, and non-coagulated ink which was not coagulated is removed from the positive electrode active surface by the squeegee 21.

[0049] Next, the substrate W comes into contact with the dots of coagulated ink between the positive electrode 11 and the pressure roller 23, so that the dots of coagulated ink formed on the positive electrode active surface are transferred onto the substrate W. In the present invention, the electrocoagulation printing apparatus is further characterized in that heating means is provided for maintaining the positive electrode active surface and the ink at a temperature ranging from about 35°C to about 60°C.

[0050] The heating means heats, e.g., the positive electrode active surface, supplies the ink onto the heated positive electrode, and transfer the heat from the positive electrode active surface to the ink, thereby to maintain the positive electrode active surface and the ink at the temperature ranging from about 35°C to about 60°C. Fig.2 shows one example of the heating means. Referring to Fig.2, the heating means 30 injects heated liquid or gas T from a hole 31 formed on the central axis of the rotating cylindrical positive electrode 11, and discharge the same from a hole 33 formed on the central axis of the electrode 11 through an interior of the cylindrical positive electrode, thereby to heat the positive electrode active surface from inside to maintain it at the temperature ranging from about 35°C to about 60°C. The ink supplied onto the heated positive electrode active surface by the ink injection means is heated on the positive electrode active surface and is maintained at the temperature ranging from about 35°C to about 60°C. The reference number 35 denotes a liquid medium accumulated in the cylindrical positive electrode when a liquid medium is used as a heating medium.

[0051] The ink is heated not only by the positive electrode active surface as described above, but also by the ink itself. This can be achieved, e.g., by heating the ink using an apparatus as shown in Fig.3, and by introducing the heated ink onto the positive electrode active surface through the ink injection means. In an ink heating apparatus 40 shown in Fig.3, an ink I introduced from an inlet port 43 to a thermostat 41 is heated up to a predetermined temperature, and is discharged from an outlet port 45 and is introduced to the ink injection means.

[0052] According to another embodiment, it is possible to heat the positive electrode active surface from outside. That is, by directing the heated liquid or gas against the positive electrode active surface, the positive electrode active surface is heated to heat the ink, thereby to maintain the positive electrode active surface and the ink at the temperature ranging from about 35°C to about 60°C.

[0053] Fig.4 shows an example of the heating means for heating the positive electrode active surface from outside. A heating means 50 is heated by a heating apparatus 53 such as an immersion heater in a water

tank 51, and this is achieved by circulating, by a high pressure pump 55, water whose temperature is maintained at a constant value. Warm water circulated through a delivery pipe 56 is directed against the cylindrical positive electrode 11 by jetting means 57 to heat the positive electrode active surface, and is returned into the water tank 51 through an outlet port 58 and a return pipe 59. The heating means may be provided alone, but it is more preferable to combine it with cleaning means.

[0054] That is, Fig.5 shows an example for heating the positive electrode by cleaning liquid. As can be seen in Fig.5, the electrocoagulation printing apparatus 1 includes the heating means 50 for heating the positive electrode active surface from outside. The cleaning liquid is heated and such cleaning liquid is sent to the cleaning means 25 and directed against the positive electrode surface, thereby to heat the surface of the positive electrode 11. The heated cleaning liquid is sent into a cleaning unit from the delivery pipe 56 by the high pressure pump 55, and is circulated through the return pipe 59.

[0055] Fig.6 is a cross section showing the outline the cleaning means 25 which cleans the positive electrode active surface and removes all the remaining coagulated ink from the positive electrode active surface. As can be seen in Fig.5, the cleaning means 25 is structured by: an elongated rotatable brush 61 extending parallel to the longitudinal axis of the cylindrical positive electrode 11 rotatable in a predetermined direction, the brush being provided with a plurality of radially extending bristles 63 having extremities contacting the positive electrode active surface 65, and being rotatable in a direction opposite to the direction of rotation of the positive electrode 11 so as to cause the bristles 63 to frictionally engage the positive electrode active surface 65; and jetting means 57, 57' for directing jets of cleaning liquid under pressure against the positive electrode active surface from one side or both sides of the brush. Each of the jetting means 57, 57' extends in parallel to the central axis of the positive electrode 11, and includes a pipe 69 having a plurality of nozzles 67 which are separated from one another. The pipe 69 is coupled to the high pressure pump 53 through a tube 71. The brush 61 rotates around the shaft 62 in a direction opposite from the rotational direction of the positive electrode 11, and the bristles 63 scrub the positive electrode active surface 65 to clean the positive electrode active surface together with the jet of the cleaning liquid.

[0056] With this cleaning means 25, the cleaning liquid is heated, and the heated cleaning liquid is directed against the positive electrode active surface to heat the positive electrode active surface, and the ink is supplied to the heated positive electrode active surface, so that the heat is transferred from the positive electrode active surface to the ink and the positive electrode active surface and the ink can be maintained at the temperature ranging from about 35°C to about 60°C.

[0057] The cleaning liquid directed against the positive electrode is once accumulated in a tub 73 in the apparatus, and overflowed from a drain tube 75, and returned into the water tank 51 through the valve 77 for circulation. Excessive cleaning liquid remaining on the positive electrode active surface 65 is removed therefrom by a squeegee roller 81 or a squeegee blade (not shown) which rotates in a direction opposite to the positive electrode 11, and a surface of the squeegee roller 81 is continuously cleaned by a brush 83 which rotates in a direction opposite to the squeegee roller 81. The squeegee roller 81 and the brush 83 are separated from the brush 61 by a partition 84. The reference number 79 denotes a discharge pipe which discharges the cleaning liquid and which is adjusted by a valve 77.

[0058] When this apparatus is actually used, in order to maintain the temperatures of the positive electrode active surface and the ink, the above described heating means should not be limited to a single means, and a plurality of heating means can be combined together. For example, a plurality of heating means can be employed to heat the positive electrode from inside and at the same time, to heat the positive electrode also from outside by the cleaning liquid. Further, means for directly heating the ink can also be employed.

[0059] Next, the electrocoagulation printing method and apparatus of the present invention will be described based on an embodiment. But the present invention should not be limited by this embodiment only.

PREFERRED EMBODIMENTS

[0060] As the electrocoagulation printing ink, there was prepared a dispersion ink including: 8.8 weight % of carbon black as coloring agent; 8.8 weight % of polyacrylamide resin (weight-average molecular weight: 250,000) as electrolytically coagulable polymer; 8.8 weight % of potassium chloride as soluble electrolyte; and water as liquid medium.

[0061] A relationship between temperature and electric conductivity of the prepared ink was measured using electric conductivity meter (CONDUCTIVITY METER DS-12 made by HORIBA, Inc.). Fig.7 shows the result.

[0062] Next, using the obtained ink, optical density of coagulated ink transferred onto the substrate was measured. Fig.5 shows the used electrocoagulation printing machine. The cleaning liquid was heated by a heating apparatus disposed in a cleaning liquid tank, such heated cleaning liquid was jetted against the positive electrode, thereby to heat the positive electrode active surface and the ink to a predetermined temperature. As oily substance for forming micro-droplets of the oily substance on the positive electrode active surface, there was used oleic acid in which about 25 weight % of metal oxide (chromium oxide) was dispersed. As substrate, a piece of Japanese newspaper was used.

[0063] Next, a voltage of 40 volts was applied between

the electrodes for a predetermined time period, and a test pattern was printed. In the printed test pattern, rectangular patched portions in which printing density is varied stepwise, characters and photograph were formed. Optical density was measured by measuring a portion having the maximum density and the patch having density of 50% using an optical density meter made by X-Rite, Inc. According to the electrocoagulation printing method of the present invention, application time of voltage is varied to vary a volume of dots of coagulated ink, thereby to vary an amount of transfer of the ink on the substrate to vary the density. Therefore, the increase of both the optical densities of both the portion having the maximum density and the patch having density of 50% can be considered as the result of improvement of the coagulating efficiency of the ink.

[0064] Procedures of the experiment were as follows: the test pattern was printed while varying the temperature of the circulated cleaning liquid stepwise at 22°C, 25°C, 30°C, 35°C, 40°C, 45°C and 48°C, and the optical density of the test pattern was measured. Fig.8 shows the result.

[0065] It can be seen from Fig.7 that the electric conductivity of the ink is increased, as the temperature is increased. Further, as can be seen from Fig.8, the optical density is enhanced as the printing temperature is increased, and the optical density has substantially the constant value at 35°C or more, and it can be seen that the coagulation efficiency is enhanced by maintaining the positive electrode active surface and the ink at the temperature ranging from about 35 to about 60°C, preferably from about 35 to about 50°C, and more preferably from about 35 to about 45°C.

Claims

1. An electrocoagulation printing method, comprising the steps of :
 - a) providing a positive electrode having an active surface, and forming a plurality of dots of colored, coagulated ink representative of a desired image on the positive electrode active surface by electrocoagulation of an electrolytically coagulable printing ink; and
 - b) bringing a substrate into contact with the dots of colored, coagulated ink to transfer the colored, coagulated ink onto the substrate from the positive electrode active surface, to thereby print the image onto the substrate; wherein the step (a) is carried out while maintaining the positive electrode active surface and the ink at a temperature of from about 35 °C to about 60 °C.
2. An electrocoagulation printing method according to claim 1, wherein the positive electrode active surface and the ink are maintained at a temperature of

from about 35 °C to about 45 °C.

3. An electrocoagulation printing method according to claim 1, wherein the positive electrode active surface and the ink are maintained at a temperature of from about 35 °C to about 60 °C by heating the positive electrode active surface and supplying the ink onto the heated electrode surface thereby to cause a transfer of heat therefrom to the ink.
4. An electrocoagulation printing method according to claim 1 or 3, wherein the electrolytically coagulable printing ink includes an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent, with the liquid medium being water and the electrolyte being selected from the group consisting of alkali metal halides and alkaline earth metal halides.
5. An electrocoagulation printing method according to claim 4, wherein the electrolyte is present in the ink in an amount of about 4.5 to about 10% by weight, based on the total weight of the ink.
6. An electrocoagulation printing method according to claim 4 or 5, wherein the electrolyte is potassium chloride.
7. An electrocoagulation printing method according to any one of claims 1, 3 or 4, wherein the substrate is water-absorbent paper.
8. An electrocoagulation printing method according to any one of claims 1, 3, 4 and 7, wherein the steps (a) and (b) are repeated several times to define a corresponding number of printing stages arranged at predetermined locations along a predetermined path, each using a coloring agent of different color, to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the substrate in superimposed relation to provide a polychromatic image.
9. An electrocoagulation printing method according to claim 8, wherein the positive electrode is a cylindrical electrode having a central longitudinal axis and rotating at substantially constant speed about the longitudinal axis, and wherein the printing stages are arranged around the positive cylindrical electrode.
10. An electrocoagulation printing method according to any one of claims 1, 3, 4, 7 and 8, wherein the step (a) is carried out by:
 - i) providing a plurality of negative electrodes electrically insulated from one another and

arranged in rectilinear alignment to define a series of corresponding negative electrode active surfaces disposed in a plane parallel to the longitudinal axis of the positive electrode and spaced from the positive electrode active surface by a constant predetermined gap, the negative electrodes being spaced from one another by a distance at least equal to the electrode gap;

ii) coating the positive electrode active surface with an oily substance to form on the surface micro-droplets of the oily substance;

iii) filling the electrode gap with the electrocoagulation printing ink;

iv) electrically energizing selected ones of the negative electrodes to cause point-by-point selective coagulation and adherence of the ink onto the oily substance-coated positive electrode active surface opposite the electrode active surfaces of the energized negative electrodes while the positive electrode is rotating, to thereby form the dots of colored, coagulated ink; and

v) removing any remaining non-coagulated ink from the positive electrode active surface.

11. An electrocoagulation printing method according to claim 10, further including the step of polishing the oily substance-coated positive electrode active surface to increase adherence of the micro-droplets onto the positive electrode active surface, prior to the step (a) (iii).

12. An electrocoagulation printing method according to any one of claims 1, 3, 4, 7, 8 and 10, further including the step of removing after the step (b) any remaining coagulated ink from the positive electrode active surface, wherein the positive electrode is rotatable in a predetermined direction and wherein any remaining coagulated ink is removed from the positive electrode active surface by providing an elongated rotatable brush extending parallel to the longitudinal axis of the positive electrode, the brush being provided with a plurality of radially extending bristles having extremities contacting the positive electrode active surface, rotating the brush in a direction opposite to the direction of rotation of the positive electrode so as to cause the bristles to frictionally engage the positive electrode active surface, and directing jets of cleaning liquid under pressure against the positive electrode active surface, from either side of the brush.

13. An electrocoagulation printing method according to claim 12, wherein the positive electrode active surface and the ink are maintained at the temperature by heating the cleaning liquid to thereby heat the positive electrode active surface upon contacting

the heated cleaning liquid and applying the ink onto the heated electrode surface to cause a transfer of heat therefrom to the ink.

14. An electrocoagulation printing apparatus, comprising: 5

a positive electrode having an active surface;
 means for supplying an electrolytically coagulable printing ink to the positive electrode; 10
 means for forming a plurality of dots of colored coagulated ink representative of a desired image on the positive electrode active surface by electrocoagulation of the ink;
 means for bringing a substrate into contact with dots of the colored coagulated ink to cause a transfer of the colored coagulated ink onto the substrate from the positive electrode active surface, to thereby print the image onto the substrate; and 20
 heating means for maintaining the temperature of the positive electrode active surface and the ink at from about 35 °C to about 60 °C.

15. An electrocoagulation printing apparatus according to claim 14, wherein the heating means heats the positive electrode active surface, supplies the ink onto the heated electrode surface to cause a transfer of heat therefrom to the ink from the positive electrode active surface thereby to maintain the temperature of the positive electrode active surface and the ink at from about 35 °C to about 60 °C. 25 30

16. An electrocoagulation printing apparatus according to claim 14 or 15, further comprising coating means for coating an oily substance on the positive electrode active surface for forming micro-droplets onto the positive electrode active surface. 35

17. An electrocoagulation printing apparatus according to any one of claims 14, 15 and 16, further comprising cleaning means for removing any remaining coagulated ink from the positive electrode active surface by cleaning the positive electrode active surface. 40 45

18. An electrocoagulation printing apparatus according to claim 17, wherein the cleaning means is structured by: a elongated rotatable brush extending parallel to the longitudinal axis of the cylindrical positive electrode rotatable in a predetermined direction, being provided with a plurality of radially extending bristles having extremities contacting the positive electrode active surface, and being rotatable in a direction opposite to the direction of rotation of the positive electrode so as to cause the bristles to frictionally engage the positive electrode active surface; and jetting means for directing jets of 50 55

cleaning liquid under pressure against the positive electrode active surface from either side of the brush, and wherein the positive electrode active surface and the ink are maintained at from about 35 °C to about 60 °C by heating the cleaning liquid by the heating means to thereby heat the positive electrode active surface by injecting the heated cleaning liquid against the positive electrode active surface and applying the ink onto the heated positive electrode surface to cause a transfer of heat therefrom to the ink.

FIG. 1

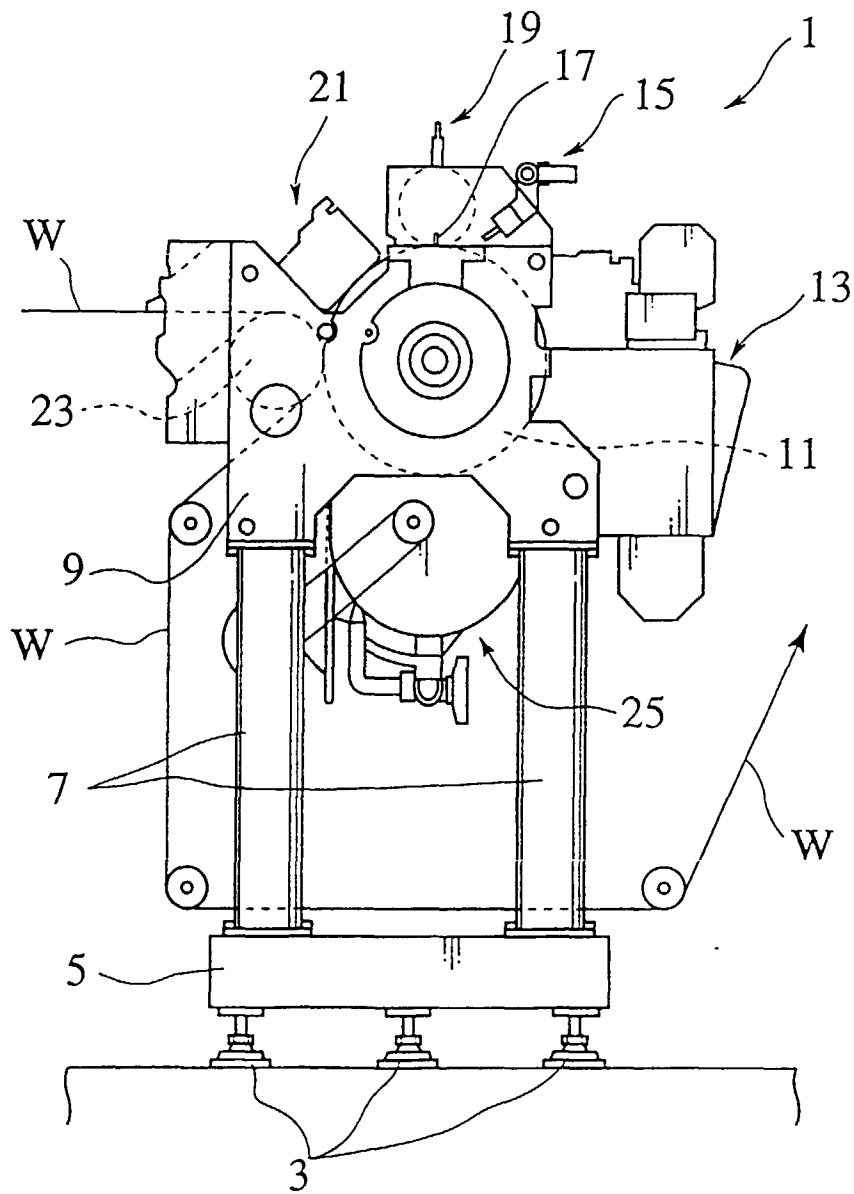


FIG. 2

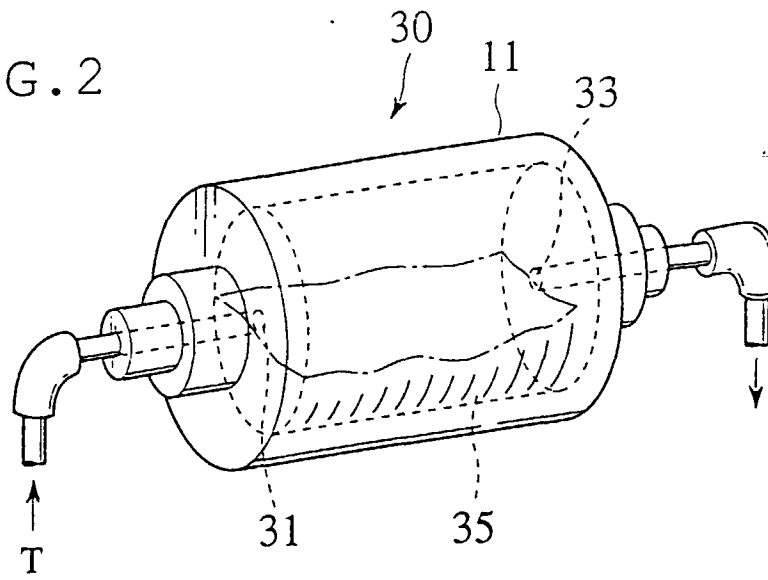


FIG. 3

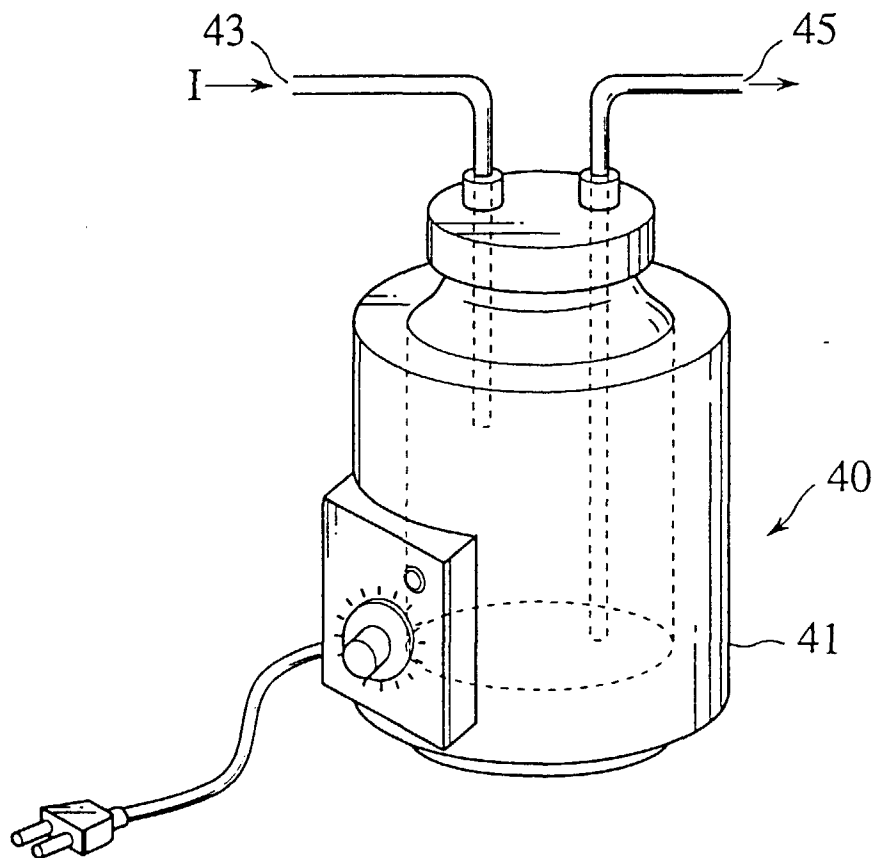


FIG. 4

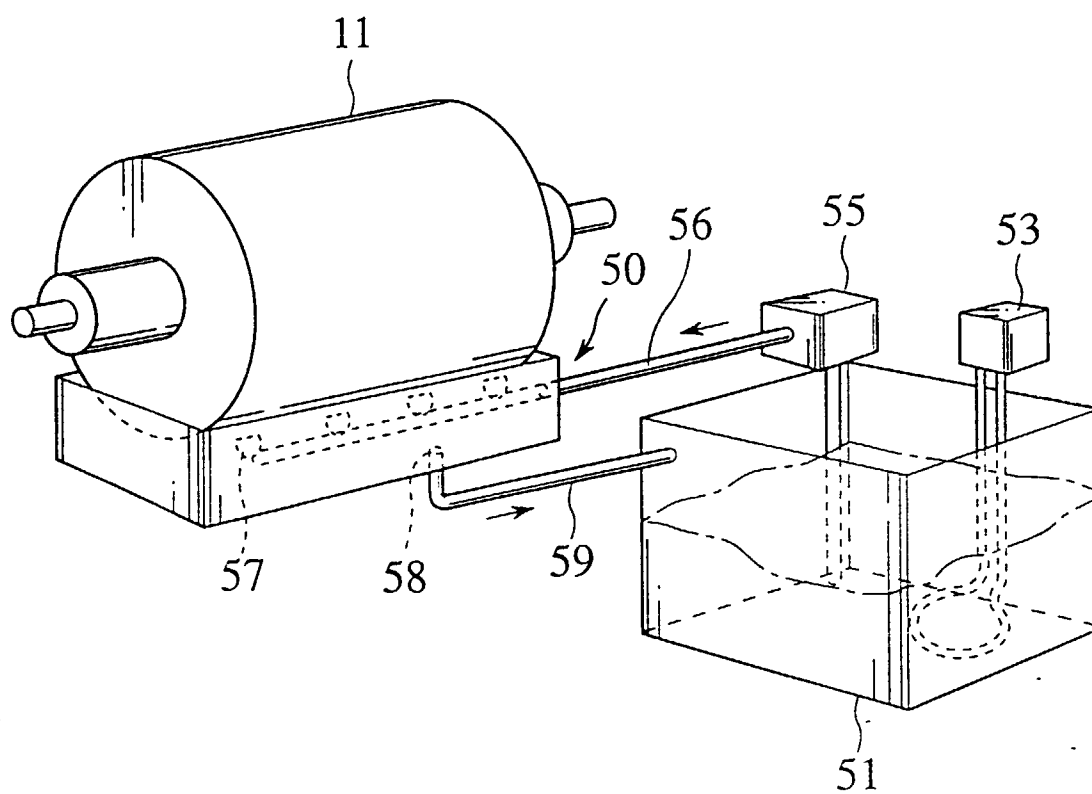


FIG. 5

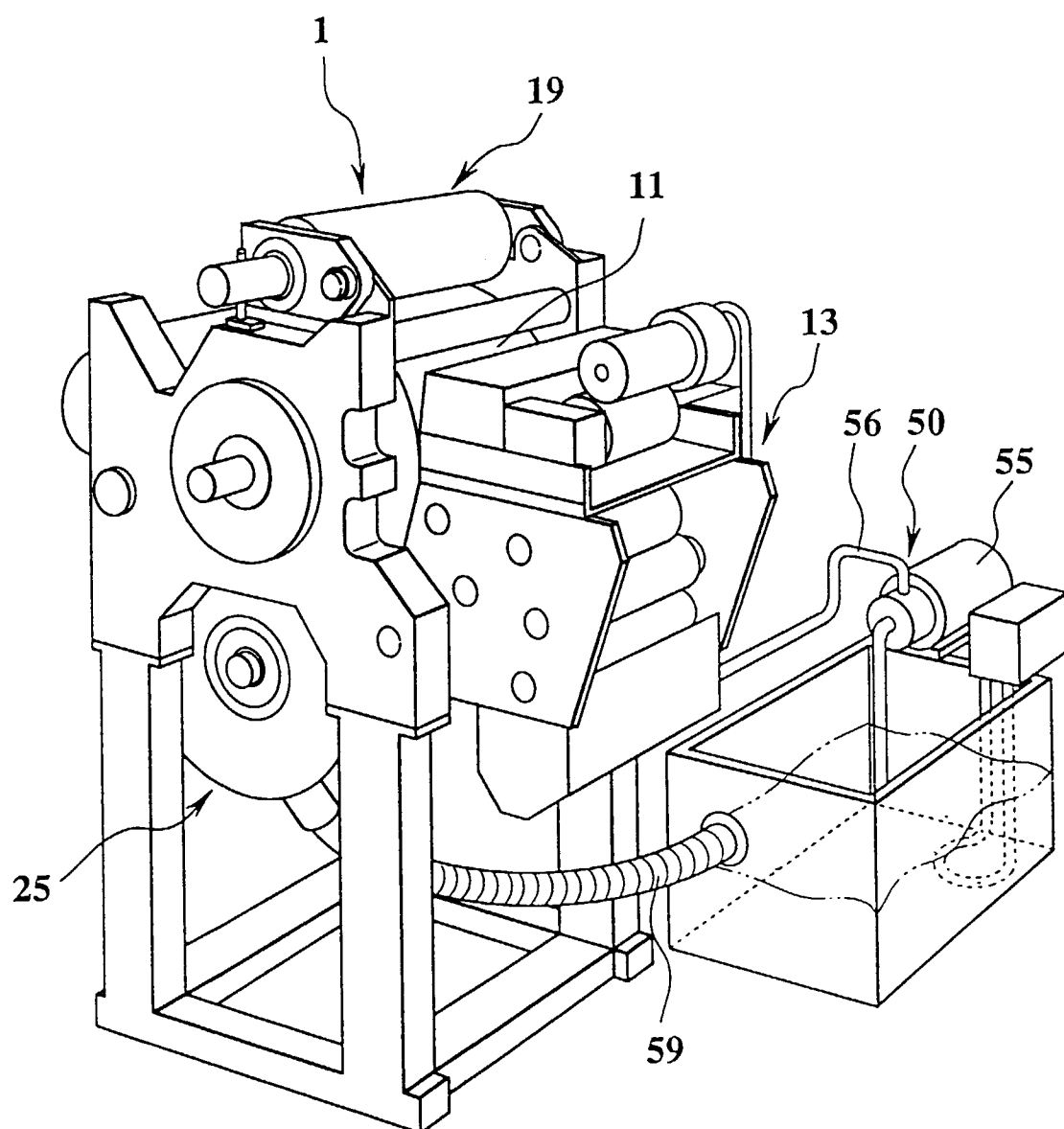


FIG. 6

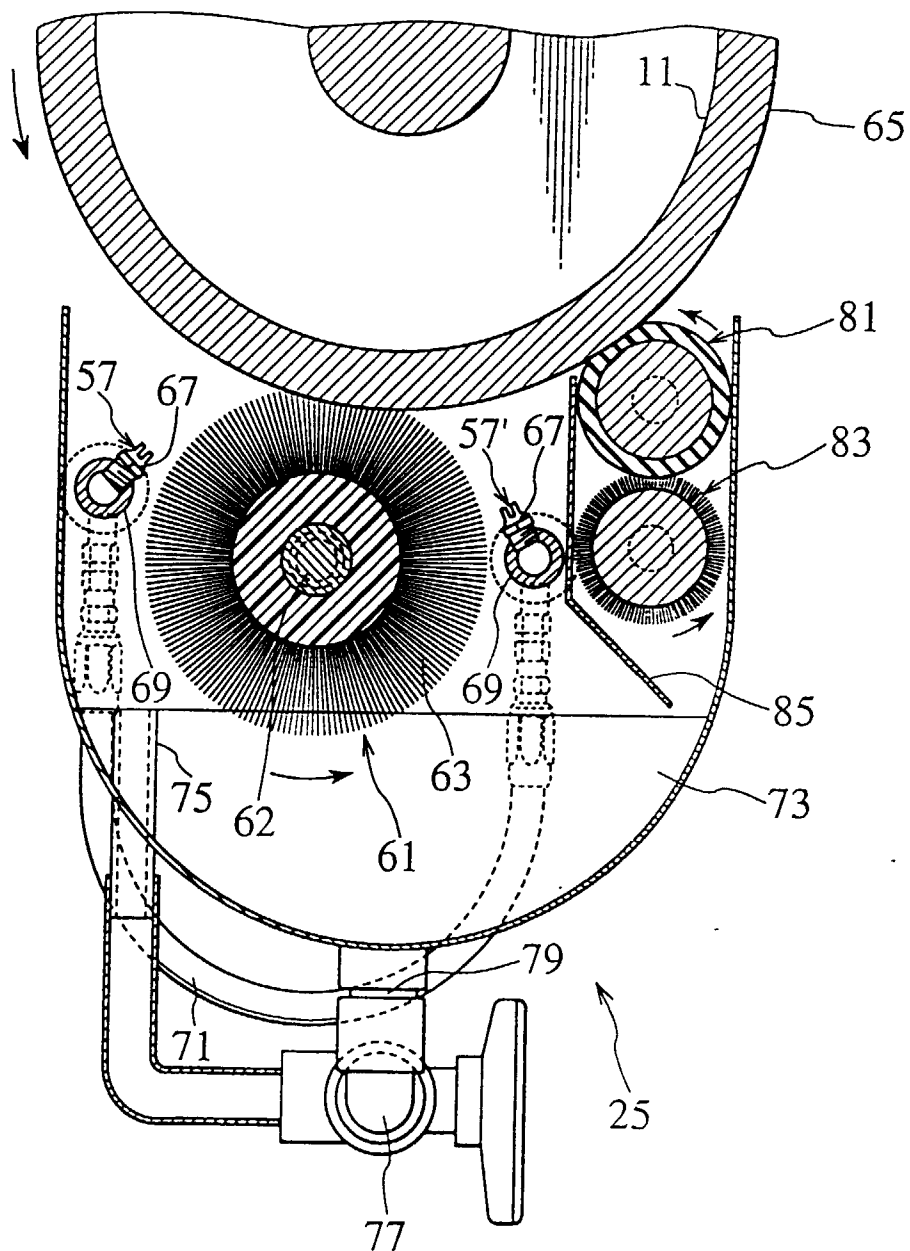


FIG. 7

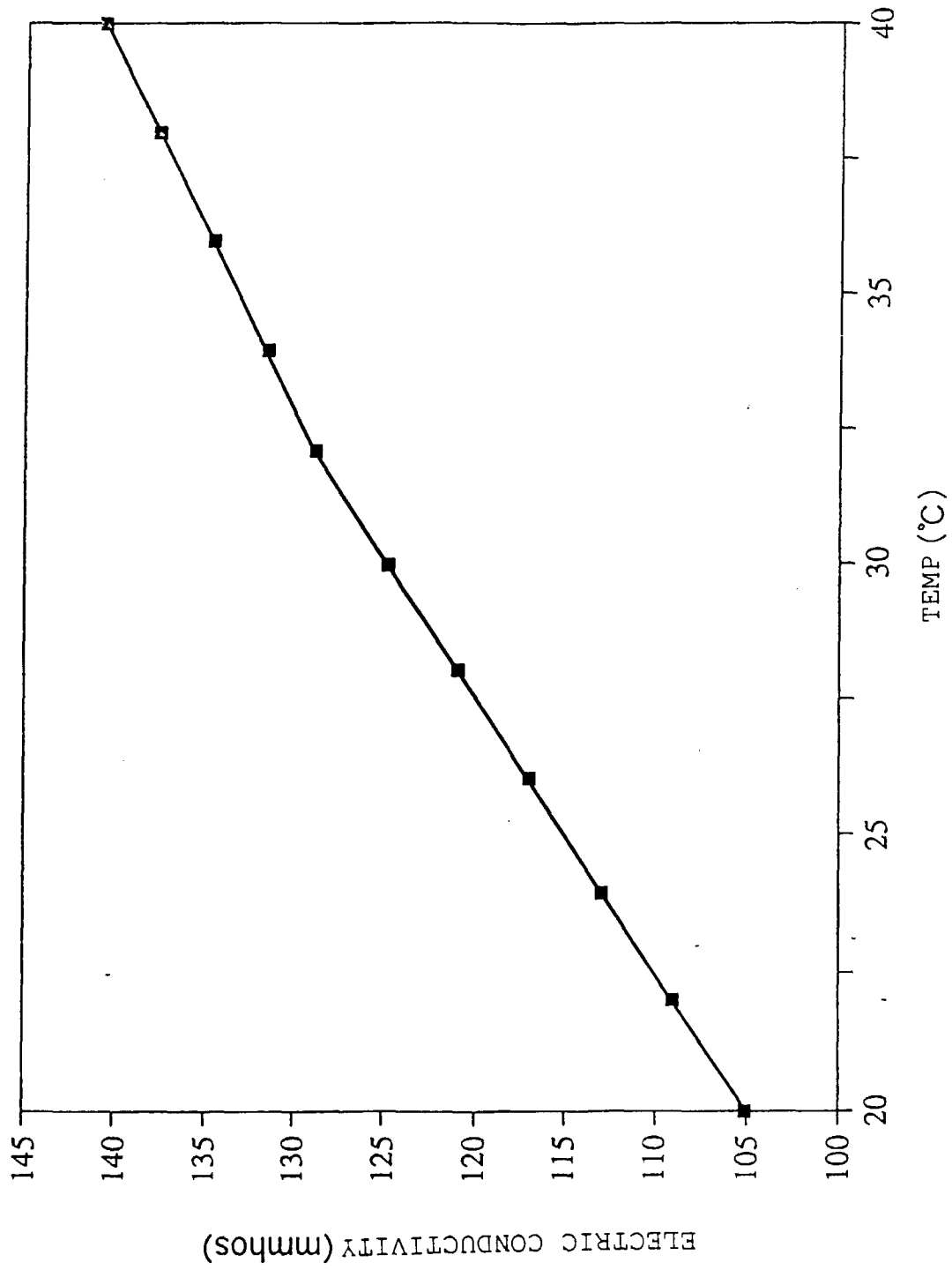
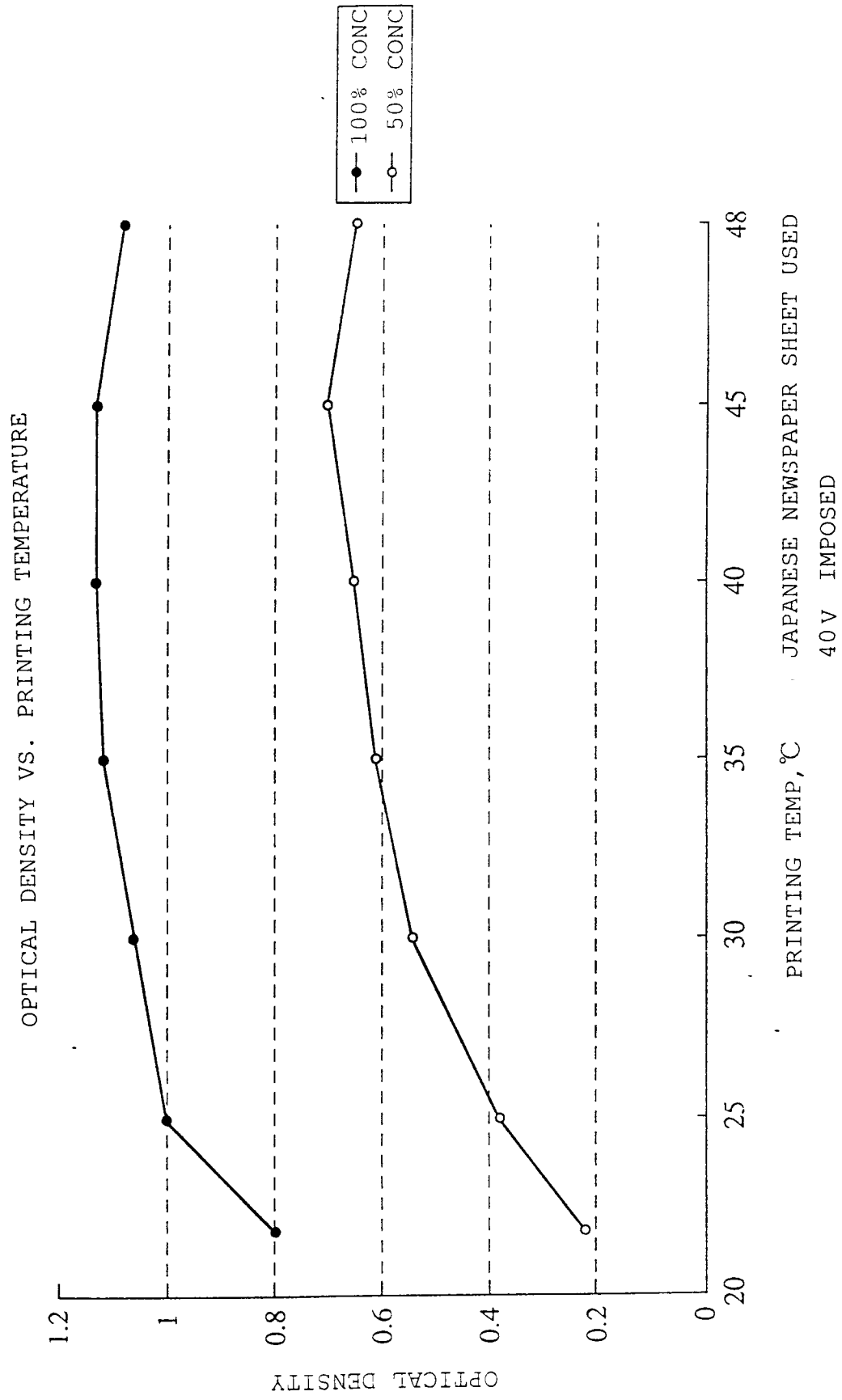


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/04903

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ B41J2/43, B41M5/20		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ B41J2/43, B41M5/20		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 54-10455, B (Adrien Castenière), May 7, 1979 (07. 05. 79), Full text (Family: none)	1-17
A	JP, 4-73386, B (Adrien Castenière), November 20, 1992 (20. 11. 92), Full text (Family: none)	1-17
A	JP, 4-504688, A (Elcorsy Inc.), August 20, 1991 (20. 08. 91), Full text (WO90/11897)	1-17
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search March 31, 1998 (31. 03. 98)		Date of mailing of the international search report April 14, 1998 (14. 04. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)