



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 153 993 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
14.11.2001 Bulletin 2001/46

(51) Int Cl.7: **C09D 11/02, B41M 5/20**

(21) Application number: **99974191.1**

(86) International application number:
PCT/JP99/06430

(22) Date of filing: **18.11.1999**

(87) International publication number:
WO 01/36548 (25.05.2001 Gazette 2001/21)

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

- **KUMADA, Hideaki, Toyo Ink Mfg. Co., Ltd.
Tokyo 104-0031 (JP)**
- **KAWASHIMA, Hiroyuki, Toyo Ink Mfg. Co., Ltd.
Tokyo 104-0031 (JP)**

(71) Applicant: **TOYO INK MFG. CO., LTD.**
Chuo-ku Tokyo 1040-0031 (JP)

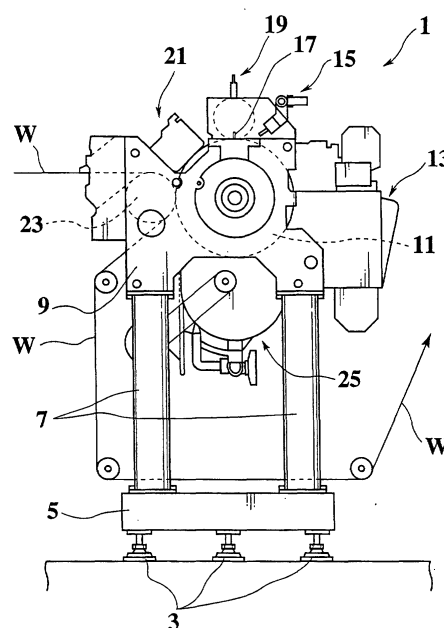
(74) Representative: **Koepe, Gerd L., Dipl.-Chem.
Koepe, Fiesser & Partner,
Radeckestrasse 43 EG
81245 München (DE)**

(72) Inventors:
• **NIZUMA, Masami, Toyo Ink Mfg. Co., Ltd.
Tokyo 104-0031 (JP)**

(54) **ELECTROCOAGULATION PRINTING INK AND ITS USE**

(57) The present invention discloses an improved electrocoagulation printing ink which can be easily removed from the surface of a cylindrical positive electrode and never causes undesirable spotted background at a non-image portion of a printed matter when a continuous printing operation is performed, a printed matter which is free from any degradation of a quality caused by spotted background, and an electrocoagulation printing method for fabricating the printed matter. The electrocoagulation printing ink contains: an acetylene glycol based surfactant, an electrolytically coagulable polymer, a coloring agent, a soluble electrolyte and a liquid medium.

FIG.1



EP 1 153 993 A1

Description**BACKGROUND OF THE INVENTION**

Field of the Invention

[0001] The present invention relates to improvements in the field of an electrocoagulation printing. More particularly, the present invention relates to an improved electrocoagulation printing ink which does not cause any undesirable spotted background at a non-image portion of a printed matter when a continuous printing operation is performed.

Description of the Related Art

[0002] According to the electrocoagulation printing, a printed matter can be directly obtained in response to a digital image signal output from a computer without requiring any plate at all. Consequently, no process of fabricating or replacing plates is necessary, thereby shortening a printing time, unlike conventional printing systems such as off-set printing, relief printing, screen printing and gravure printing. Furthermore, a water-based ink can be used in this printing system, so that the printing system is excellent from the viewpoint of prevention of a danger of atmospheric pollution or a fire, safety and health during the operation or the like in comparison with a printing system in which an oily ink is used.

[0003] Electrocoagulation printing methods and apparatuses are disclosed in U.S. Patent Nos. 4,895,629 (registered on January 23, 1990), 5,538,601 (registered on July 23, 1996), 5,693,206 (registered on December 2, 1997) and the like.

[0004] The electrocoagulation printing method has the following steps. The surface of the positive electrode is cleaned and coated with an oily substance. Then, dots of coagulated ink representing an image are formed on the surface by electrocoagulation of a printing ink, that is, electrocoagulation ink containing an electrolytically coagulable polymer. The printing ink which has not been coagulated and remains on the surface of the positive electrode, i.e., a non-coagulated ink is removed, and thus, the exposed dots of the coagulated ink are transferred onto a substrate, so that the image is printed on the substrate.

[0005] Therefore, the electrocoagulation printing apparatus comprising: revolving a cylindrical positive electrode which has a passivated surface; a positive electrode surface cleaning means; oily substance applying means; printing ink supplying means; a plurality of negative electrodes spaced apart from the positive electrode by a fixed distance; non-coagulated ink removing means; and a transferring means, for transferring the dots of the coagulated ink from the positive electrode onto the substrate.

[0006] After the printing ink is electrolytically coagulated, the non-coagulated ink is removed from the surface of the cylindrical positive electrode, for example, by scraping the surface with a soft rubber squeegee. When the continuous printing operation is performed to extend a printing time, it becomes difficult to completely remove the non-coagulated ink from the surface of the positive electrode by using the squeegee. As a result, undesirable stains (background), in particular, spotted background are caused at a non-image portion by the non-coagulated ink remaining at the surface of the positive electrode, thereby arising a problem of the degradation of the quality of an obtained printed matter. As a solution for this problem, if the non-coagulated ink is to be completely removed from the surface of the positive electrode by increasing the hardness of the squeegee or the pressure of the squeegee against the surface of the cylindrical positive electrode, there has arisen a problem that the dots themselves of the coagulated ink are unexpectedly removed or damaged, to thus degrade the quality of the obtained printed matter. It was a cumbersome task to remove the non-coagulated ink to such an extent as to prevent any generation of the spotted background and adjust the squeegee to such an extent as not to damage the dots of the coagulated ink.

SUMMARY OF THE INVENTION

[0007] An object of the present invention is to solve the above-described problems which have not been solved by means of the conventional electrocoagulation printing ink in the prior art. Namely, an object of the present invention is to provide an improved electrocoagulation printing ink which can be easily removed from the surface of a cylindrical positive electrode and does not cause undesirable spotted background at a non-image portion of a printed matter when a continuous printing operation is performed, a printed matter which is free from any degradation of a quality caused by spotted background, and an electrocoagulation printing method for fabricating the printed matter.

[0008] In view of the above-described current situations, the present inventors have earnestly studied and found that an electrocoagulation printing ink containing an acetylene glycol based surfactant can be easily removed from the surface of a cylindrical positive electrode in a non-coagulated state, so that the quality of a printed matter can be prevented from being degraded by spotted background, and at last, they have reached to the present invention.

[0009] Specifically, the present invention relates to an electrocoagulation printing ink containing: an acetylene glycol based surfactant; an electrolytically coagulable polymer; a coloring agent; a soluble electrolyte; and a liquid medium.

[0010] Moreover, the present invention relates to a printed matter printed with the above-described electrocoagulation printing ink.

[0011] Furthermore, the present invention relates to an electrocoagulation printing method using the above-described electrocoagulation printing ink.

[0012] The expression "electrocoagulation printing method" as used herein refers to an entire printing process by which an image is reproduced by electrocoagulation of printing ink containing electrolytically coagulable polymer, and then, the image thus reproduced is transferred onto a substrate. The entire printing process thus includes the steps of:

(a) cleaning the positive electrode surface; (b) coating the positive electrode surface with micro-droplets of an oily substance; (c) filling the electrode gap between the positive electrode and a negative electrode with the printing ink; (d) applying a voltage to selected negative electrodes, representative of a desired image, so as to reproduce dots of coagulated ink on the surface of the positive electrode coated with the micro-droplets of an oily substance; (e) removing the printing ink which has not been coagulated, i.e., a non-coagulated ink from the surface of the positive electrode; and (f) transferring, onto the substrate, the dots of the coagulated ink reproduced on the surface of the positive electrode.

[0013] The expression "electrocoagulation of the printing ink" as used herein refers only to step (d) of the above process, which involves: applying the voltage to selected negative electrodes, representative of the desired image, so as to break a passive oxide film on the positive electrode surface and to release multivalent metal ions from the positive electrode surface; coagulating the printing ink by a chemical bond between the multivalent metal ions and the electrolytically coagulable polymer contained in the printing ink; and thus, reproducing the dots of the coagulated ink on the positive electrode surface. The multivalent metal ions released from the positive electrode surface are trivalent irons or aluminum ions in the case where, for example, the positive electrode made of stainless steel or aluminum is used in the electrocoagulation printing method.

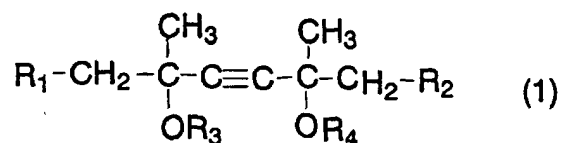
BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Fig. 1 shows an example of an electrocoagulation printing apparatus in which an electrocoagulation printing ink according to the present invention is utilized.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] A description will be given in details of the present invention. Here, "an ink" all used in the description below refers "an electrocoagulation printing ink."

[0016] An acetylene glycol based surfactant for use in the ink according to the present invention is a compound having at least one triple bond of carbon-to-carbon and two hydroxyl groups, and can be used individually or in combination of two kinds or more. The acetylene glycol based surfactant is preferably a nonionic acetylene glycol based surfactant expressed by a chemical formula (1), as follows:



where R_1 and R_2 each are $\text{CH}_3\text{-CH}_2$ or $\text{CH}_3\text{-CH}(\text{CH}_3)$; R_3 is $(\text{CH}_2\text{CH}_2\text{O})_m\text{-H}$; R_4 is $(\text{CH}_2\text{CH}_2\text{O})_n\text{-H}$; and $m+n$ is an integer ranging from 0 to 50, and more preferably, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, wherein R_1 and R_2 in the chemical formula (1) each are $\text{CH}_3\text{-CH}(\text{CH}_3)$ and $m+n$ is 0.

[0017] The nonionic acetylene glycol based surfactant expressed by the chemical formula (1) is available from manufacturers, for example, Air Products Japan Inc. or Kawaken Fine Chemicals Co., Ltd.

[0018] The amount of the acetylene glycol based surfactant is preferably 0.01% by weight to 2% by weight based on the total weight of the ink. If the amount is less than 0.01% by weight, the effect of preventing generation of spotted background is weak, thereby showing a tendency to make it difficult to obtain a printed matter of an excellent quality. In contrast, if the amount is more than 2% by weight, the optical density at a non-image portion of a printed matter is tended to become slightly high, and further, it is difficult to transfer dots of coagulated ink onto the substrate, thereby showing a tendency of a decrease in density of a printed image, although it is possible to prevent any generation of spotted background.

[0019] The acetylene glycol based surfactant may be added to the ink by a known method in the prior art. For example, the acetylene glycol based surfactant may be added to the ink either at the time of ink preparation or immediately before a printing operation.

[0020] An electrolytically coagulable polymer used in the ink is capable of making chemical bonds with multivalent metal ions and preferably contains a functional group such as an amido group, an amino group and a carboxyl group. The polymer has a weight average molecular weight preferably between about 10,000 and about 1,000,000, or more preferably between 100,000 and 600,000. The weight average molecular weight of the electrolytically coagulable polymer can be determined by a gel permeation chromatography (detector: light scattering meter) or calculated using a relationship between the limiting viscosity of the polymer and the weight-average molecular weight thereof. If the weight average molecular weight of the electrolytically coagulable polymer is less than about 10,000, the ink is hardly coagulated, thereby decreasing the density of the printed matter. In contrast, if the weight average molecular weight of the electrolytically coagulable polymer is more than 1,000,000, the viscosity of the ink is increased to show a tendency of degraded workability at the time of the ink preparation or the printing operation. The basic structure of the electrolytically coagulable polymer is preferably a straight-chain structure, but it may be branched.

[0021] Examples of suitable polymers include natural polymers such as albumin, gelatin, casein and agar and synthetic polymers such as polyacrylic acid, modified polyacrylic acid, polyacrylamide, modified polyacrylamide and polyacrylic acid hydrazide. The electrolytically coagulable polymer can be used individually or in combination of two kinds or more. The polymer is preferably contained in an amount of about 4% to about 15% by weight, and more preferably, in an amount of about 6% to about 12% by weight, based on the total weight of the ink. If the amount of the polymer is less than about 4% by weight, there is a tendency of a decrease in density of the coagulated ink transferred onto the substrate. In contrast, if the amount of the polymer is more than about 15% by weight, the viscosity of the ink is increased to show a tendency of degraded workability at the time of the ink preparation or the printing operation.

[0022] A preferable one of the polymers is modified polyacrylamide, for example, nonionic, anionic and cationic acrylamide polymers. The modified polyacrylamide is available from manufacturers, for example, Arakawa Chemical Industries, Ltd., Mitsubishi Chemical Corporation, Harima Chemicals, Inc., Mitsui Toatsu Chemicals, Inc., Mitsui Cytec Ltd., Sanyo Chemical Industries, Ltd. and the like. A more preferable one of the electrolytically coagulable polymers is a linear anionic acrylamide polymer, and specifically, it is ACCOSTRENGTH 86 available from Mitsui Cytec Ltd.

[0023] A coloring agent used in the ink according to the present invention includes pigments and dyes which are used for general printing inks, coating materials and recording agents.

[0024] The pigments can be organic pigments or inorganic pigments.

[0025] Examples of the organic pigments include azo pigment, phthalocyanine pigment, anthraquinone pigment, perylene pigment, perinone pigment, quinacridone pigment, thioindigo pigment, dioxazine pigment, isoindolinone pigment, quinophthalone pigment, azomethineazo pigment, diketopyrrolopyrrole pigment and isoindoline pigment.

[0026] For an yellow ink and a magenta ink, the use of azo pigment is preferable. For example, Permanent Yellow DGR or DHG and Permanent Rubine F6B or L6B available from HOECHST are preferably used for the yellow ink and the magenta ink, respectively. For a cyan ink, the use of copper-phthalocyanine pigment is suitable. For example, Heliogen Blue D7072DD available from BASF is preferably used for the cyan ink.

[0027] Examples of the inorganic pigments include carbon black, titanium oxide, zinc oxide, zinc sulfide, barium sulfate, calcium carbonate and chromium oxide. For a black ink, the use of carbon black is preferable. Especially, the use of carbon black having an oil absorption of 65 to 120 ml/100 g and an average particle diameter of 35 to 100 nm enables one to produce printed matters colored in bluish deep blackness and having high density. As a carbon black, for example, use can be made of Carbon Black Monarch (a registered trade mark) 120 which has an oil absorption amount of 72 ml/100 g and an average particle size of 75 nm available from CABOT CORP.

[0028] The pigment can be used individually or in combination of two kinds or more for the purpose of adjustment of the hue and the density. Moreover, the pigment may be used in the state of either aqueous slurry or dried powder pulverized by drying the slurry, for example, by spray-drying.

[0029] These pigments are used in an amount necessary in producing the dots of coagulated ink by electrocoagulation with a sufficient density, preferably in an amount of about 4 to about 20% by weight based on the total weight of the ink.

[0030] Examples of the dyes include acid dye, basic dye, direct dye, reactive dye, disperse dye and metal-containing dye.

[0031] The pigment and the dye may be used together for the purpose of adjustment of the hue and the density. Here, since the use of the dye may degrade the dispersion stability of the pigment or the resistance of a printed image against water and light, the content of the dye is preferably 40% by weight or less of the pigment, more preferably, 25% by weight or less.

[0032] When the coloring agent used in the ink of the present invention is a pigment, a dispersant may be used in order to stably disperse the pigment in a liquid medium. Moreover, the pigment can be stably dispersed in a liquid medium by using the above-described electrolytically coagulable polymer. In this case, the electrolytically coagulable

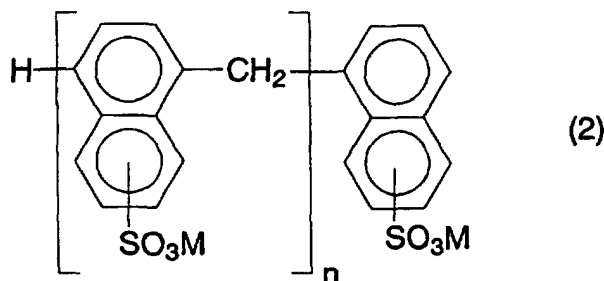
polymer can be dispersed individually, and further, the dispersant may be used together in order to disperse the pigment more stably.

[0033] As the dispersant, anionic, nonionic, cationic or amphoteric surfactant may be used.

[0034] The dispersant is preferably contained in the ink in an amount of about 0.05% to about 5% by weight, or more preferably, in an amount of about 0.1% to about 2% by weight, based on the total weight of the ink. When the amount of the dispersant is less than 0.05% by weight, the shelf life of the ink tends to decrease, whereas when the amount of the dispersant is more than 5% by weight, the density of the coagulated dots transferred onto substrate tends to decrease.

[0035] A preferable dispersant is an alkali metal salt of a naphthalenesulfonic acid-formaldehyde condensate, and more preferably, a compound expressed by a chemical formula (2). Among them, a compound expressed by the chemical formula (2), where M is sodium and n ranges from 5 to 12, is preferable.

[0036] The alkali metal salt of the naphthalenesulfonic acid-formaldehyde condensate is available from manufacturers, for example, Kao Corporation, Sanyo Chemical Industries, Ltd., SAN NOPCO Ltd., Dai-Ichi Kogyo Seiyaku Co., Ltd., Kyoeisha Chemical Co., Ltd., Toho Chemical Industry Co., Ltd, Boehme Filatex Canada Inc. and the like. The compound specified by the formula(2) in which M is sodium and n is 7, is sold by Boehme Filatex Canada Inc. under the trade mark Cloperse 2500 as a aqueous solution, wherein its effective ingredient is about 42% and the average molecular weight of the compound is about 2000.



where M is an alkali metal and n is an integer ranging from 2 to 15.

[0037] A soluble electrolyte used in the ink is added in order to increase an electric conductivity of the ink and cause a desired breakdown of passive oxide film on the positive electrode surface. Preferred electrolytes include halide, especially chloride. Examples of alkali metal halides and alkaline earth metal halides include lithium chloride, sodium chloride, potassium chloride and calcium chloride. Use can also be made of ammonium chloride, nickel chloride, copper chloride and manganese chloride.

[0038] The soluble electrolyte can be used individually or in combination of two kinds or more.

[0039] An electric conductivity of the ink ranges preferably from 1 to 200mS/cm (at 25°C). When the electric conductivity of the ink is under 1mS/cm, the optical density of the coagulated ink transferred onto the substrate decreases. Accordingly, the soluble electrolyte is added in such an amount that the electric conductivity of the ink falls within the above range. In general, the soluble electrolyte is preferably contained in an amount of about 5 to about 10% by weight, or more preferably in an amount of about 6 to about 9% by weight, based on the total weight of the ink.

[0040] Water is preferably used as the liquid medium, which dissolves or disperses the acetylene glycol based surfactant, the coloring agent, the electrolytically coagulable polymer and the soluble electrolyte to provide desired ink.

[0041] The ink may contain a sequestering agent for complexing multivalent metal ions. The multivalent metal ions are an essential component for reproducing the dots of the coagulated ink in the electrocoagulation printing. However, if the multivalent metal ions are present in the ink before the step (d), the electrolytically coagulable polymer in the ink and the multivalent metal ions are chemically bonded to each other before the printing ink is electrocoagulated in the step (d), thereby increasing the viscosity of the ink. The viscosity of the ink increases depending on the concentration of the multivalent metal ions. Therefore, in the case where the concentration of the multivalent metal ions is high, the ink is turned to a gel state.

[0042] The multivalent metal ions may be contained in ingredients to be used for the ink, or may be introduced during the ink preparing process. Otherwise, since a small amount of the coagulated ink is also removed together with the non-coagulated ink in the case where the non-coagulated ink is removed from the surface of the positive electrode by scraping the surface of the positive electrode by a soft rubber squeegee as one example of a non-coagulated ink removing device used in the step (e), and then, the removed non-coagulated ink is recycled back to the ink discharge unit, the ink recycled contains a small amount of the multivalent metal ions released from the surface of the positive electrode. The concentration of the multivalent metal ion in the ink supplied from the ink discharge unit may become

higher as the electrocoagulation printing time becomes longer.

[0043] If the concentration of the multivalent metal ions, for example, ferric ions in the ink is greater than about 25 ppm, the ink is too viscous for proper working and, at about 140 ppm, there is gelation of the ink. In order to prevent any undesirable increase in viscosity of the ink, the sequestering agent can be added to the ink.

[0044] If the amount of the sequestering agent is small with respect to the concentration of the multivalent metal ions such as the ferric ions in the ink, the concentration of the ions exceeds 25 ppm, thereby causing an increase in viscosity of the ink. Consequently, the sequestering agent is used in such an amount as to form a complex with the multivalent metal ions such as the ferric ions in the ink and maintain the state in which the concentration of the ions becomes about 20 ppm or less, more preferably, about 15 ppm or less.

[0045] In contrast, if the sequestering agent is excessively added with respect to the multivalent metal ions such as the ferric ions in the ink, a great deal of the sequestering agent will remain in the ink, although the ferric ions are substantially completely turned into complexes. The sequestering agent remaining in the ink forms complexes with the multivalent metal ions as an essential component for forming the dots of the coagulated ink eluted from the surface of the positive electrode by the breakdown of the passivated coating film in the step (d), and therefore, it adversely affects the formation of a chemical bond between the multivalent metal ions and the electrolytically coagulable polymer contained in the ink. If the adverse affection is markedly large, the density of the dots of the coagulated ink transferred onto the substrate is decreased, and further, the dots themselves may not be reproduced. As a result, the sequestering agent is contained in such an amount as not to adversely affect the chemical bond between the multivalent metal ions and the electrolytically coagulable polymer, which is generated at the time of the electrocoagulation of the printing ink.

[0046] Thus, it is preferable that the sequestering agent is contained within the range from such an amount as to form a complex with the multivalent metal ions such as the ferric ions in the state in which the concentration of the ion in the ink before the step (d) becomes about 20 ppm or less, more preferably, about 15 ppm or less, to such an amount as to achieve the state in which the chemical bond between the multivalent metal ions released from the surface of the positive electrode at the time of the electrocoagulation of the printing ink and the electrolytically coagulable polymer can be sufficiently generated. Moreover, the amount depends upon the concentration of the multivalent metal ions in the ink, as well as, the type of the sequestering agent which is used, and further, depends upon the type and the amount of the electrolytically polymer contained in the ink.

[0047] The sequestering agent used is preferably a compound capable of forming ring structures incorporating metal ions as central metal atoms. Such a ring formation increases the stability of the metal-sequestering agent bonding. A preferred class of sequestering agents comprises polyaminocarboxylic acids and their salts. Examples of polyaminocarboxylic acids include ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IDA), hydroxyethyliminodiacetic acid (HIDA), ethylene-bis(hydroxyphenyl)glycine (EHPG), hydroxyethyl-ethylenediamine-triacetic acid (HEDTA), nitrilotriacetic acid (NTA), ethylene-bis(oxyethylenenitrilo)tetraacetic acid (EGTA), cyclohexanediaminetetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DTPA), and triethylenetetraminehexaacetic acid (TTHA). The sequestering agents can be used individually or in combination. Particularly preferred sequestering agents are EDTA and its salts which are readily available at low cost. These sequestering agents are preferably contained in an amount of about 0.01 to about 0.3% by weight, or more preferably in an amount of about 0.01 to 0.2% by weight, based on the total weight of the ink.

[0048] The sequestering agent may be added to the ink by a known method in the prior art. For example, the sequestering agent may be added at the time of the ink preparation or immediately before or during the printing operation. In the case of long term printing in the electrocoagulation printing, the amount of metal ions in the ink more increases in contrast to the case of short term printing as aforementioned. Hence it is preferable that the amount of the sequestering agent added to the ink at the beginning of the printing operation should be different from that of the sequestering agent added to the ink which may be added during the printing operation.

[0049] Hereinafter, the ink used at the beginning of the printing operation is referred to as "starting ink," in contrast, the ink added during the printing operation is referred to as "replenishing ink." When the ink is used as the starting ink, the sequestering agent is contained in the ink preferably in amount of from 0 to 0.2% by weight, more preferably in amount of from 0.01 to 0.15% by weight, based on the total weight of the ink. In contrast, when the ink is used as replenishing ink, the sequestering agent is contained in the ink preferably in amount of from 0.05% to 0.3% by weight, more preferably, in amount of from 0.1 to 0.3% by weight, based on the total weight of the ink, considering that the multivalent metal ions increased during the printing operation are turned into complexes.

[0050] The ink according to the present invention preferably contains biocidal agents for preventing the growth of bacteria or molds. Examples of preferable biocidal agents include sodium dehydroacetate, sodium benzoate, sodium pyridinethion-1-oxide, zinc pyridinethion-1-oxide and amine salts of 1,2-benzisothiazoline-3-on or 1-benzisothiazoline-3-on. For example, use can be made of a biocidal agent sold by GRAY PRODUCTS under the trademark PARMETOL K-50. The biocidal agent is preferably contained in the ink in an amount of 0.01 to 2% by weight, or more preferably in amount of about 0.01 to 1% by weight, based on the total weight of the ink. The biological agent may be used individually or in combination of two kinds or more according to the kind of a bacterium or a mold.

[0051] Other than the above compounds, various additives such as infrared-ray absorbing agents, UV-ray absorbing agents, perfumes, antioxidants, anti-foaming agents, silane coupling agents, plasticizers, flame retardants, moisture retentive agents, and organic solvents may be optionally added to the ink of the present invention as required.

[0052] The ink according to the present invention can be prepared by dissolving and/or dispersing the acetylene glycol based surfactant, the electrolytically coagulable polymer, the coloring agent and the soluble electrolyte, and other additives such as the sequestering agent, as required, in the liquid medium.

[0053] In the case where the pigment is used as the coloring agent, it is preferable that the ink is prepared as follows: a pigment dispersion is prepared in advance by dispersing the pigment in the liquid medium with a dispersant and/or the electrolytically coagulable polymer, and then, the soluble electrolyte and the acetylene glycol based surfactant, and the electrolytically coagulable polymer, the liquid medium, the sequestering agent or the biocidal agent, as required, are added to the resulting pigment dispersion. The particle size distribution of the pigment in the pigment dispersion can be adjusted by appropriately adjusting the size of crushing media by a dispersing machine, the filling rate of the crushing media, a dispersing time, the discharging speed of the pigment dispersion, the viscosity of the pigment dispersion or the like. For the dispersion, a generally used dispersing machine such as a roller mill, ball mill, pebble mill, attritor and sand mill may be used.

[0054] In the case where bulk particles or bubbles are contained in ink, it is desirable to remove them by filtration, deaeration and the like, since they hinder electrocoagulation of the ink and decrease an image quality. Any conventionally known filter and deaeration may be used.

[0055] The hydrogen ion concentration (pH) of the ink produced in the above method is preferably in a range from about 3 to about 8, more preferably from about 3 to about 6 when measured at 25 °C. When the pH is out of the range from about 3 to about 8, the density of the coagulated ink transferred onto a substrate decrease. In order to adjust the pH of the ink, conventionally known acid or alkali such as hydrochloric acid, sulfuric acid, acetic acid, sodium hydroxide, potassium hydroxide or ammonium hydroxide may be used.

[0056] The viscosity of the prepared ink preferably ranges from about 100 to about 1500 mPa·s (cps) at 30 °C. If the viscosity of the ink is lower than 100 mPa·s (cps), the density of the coagulated ink transferred onto a substrate decrease; in contrast, if it is higher than 1500 mPa·s (cps), the workability at the time of the ink preparation or during the printing operation tends to be deteriorated. The viscosity of the ink can be adjusted by appropriately selecting the types or amounts of the ingredients to be used such as the electrolytically coagulable polymer, the coloring agent or the liquid medium. In the case where the pigment is used as the coloring agent, the viscosity of the ink may be adjusted by adjusting the particle size and particle size distribution of the pigment in the ink.

[0057] A preferred ink of the present invention consists of an aqueous liquid dispersion having a pH of about 3 to about 6 and containing about 0.01 to about 2% by weight of a nonionic acetylene glycol based surfactant expressed by the chemical formula (1), about 4 to about 15% by weight of an anionic acrylamide polymer, about 4 to about 20% by weight of a pigment, about 5 to about 10% by weight of an alkali metal halide, about 60 to about 80% by weight of water, about 0.01 to about 0.3% by weight of a polyaminocarboxylic acid or its salt and about 0.01 to about 2% by weight of biocidal agent, based on the total weight of the ink.

[0058] Next, a method for using ink of the present invention will be explained.

[0059] Fig. 1 is a schematic illustration of an electrocoagulation printing apparatus 1 for the printing using the ink of the present invention. The apparatus 1 is provided with a base plate 5 mounted on a plurality of foot sections 3, and a plurality of flames 7 extending upward is mounted on the base plate 5. Furthermore, a pair of vertical plates 9 is disposed at the upper portions of the flame 7. A revolving cylindrical positive electrode 11, which can be freely rotated by a driving motor (not shown), is sandwiched between the paired vertical plates 9. The positive electrode 11 extends in a direction vertical to the paper in Figure 1 and has an active surface having a passive oxide film.

[0060] The electrocoagulation printing apparatus 1 also comprises: a coating means 13 along the positive electrode 11 for applying an oily substance to the positive electrode active surface to form micro-droplets of an oily substance on the positive electrode active surface; an ink supplying means 15 having a temperature adjusting means (not shown), for supplying the ink of the present invention onto the positive electrode; a print head 19 having negative electrodes 17 which forms, on the positive electrode active surface, a plurality of dots of colored, coagulated ink representative of a desired image by the electrocoagulation of the ink; and a removing means 21 such as a squeegee for removing non-coagulated ink from the positive electrode active surface. The electrocoagulation printing apparatus 1 also comprises a pressure roller 23 as a means by which the resulting plurality of dots of the colored, coagulated ink formed on the positive electrode active surface and representative of a desired image are contacted with a substrate W to cause transfer of the dots of the colored, coagulated ink onto the substrate from the positive electrode active surface, thereby printing the image on the substrate.

[0061] A cleaning means 25 for cleaning the positive electrode active surface to remove any remaining coagulated ink from the positive electrode active surface is disposed below the positive electrode 11.

[0062] According to such a structure, micro-droplets of an oily substance is applied by the coating means 13 on the active surface of the revolving positive electrode 11 and the ink of the present invention is then supplied to the gap

defined between negative electrodes 17 and the positive electrode 11 by the ink supplying means 15. The supplied ink forms dots of coagulated ink by electrical energization of the positive and negative electrodes and the non-coagulated ink is removed from the positive electrode active surface by a squeegee 21.

[0063] Then, the dots of coagulated ink, formed on the positive electrode active surface, are contacted with a substrate W at the position between the positive electrode 11 and the pressure roller 23 so as to transfer the dots of coagulated ink onto the substrate W and thereby imprint the substrate W.

[0064] A multicolor printing can be achieved by preparing a desired number of electrocoagulation printing apparatus 1 shown in Figure 1 and sequentially printing with electrocoagulation printing inks of desired colors in each electrocoagulation printing apparatus. For instance, process printing can be carried out by arranging four electrocoagulation printing apparatuses 1 shown in Figure 1 in tandem and printing sequentially using yellow, cyan, magenta, and black inks in each apparatus.

[0065] Moreover, the electrocoagulation printing apparatus for the printing using the ink according to the present invention may be a center drum type printing apparatus disclosed in U.S. Patent No. 5,538,601 (registered on July 23, 1996). In this printing system, a printing stage comprising a positive electrode surface cleaning means, an oily substance coating means, an ink supplying means, a plurality of negative electrodes spaced apart from a positive electrode by a fixed distance, a non-coagulated ink removing means and a transferring means is disposed around a rotatable cylindrical positive electrode having a passivated surface. For instance, four printing stages are disposed around a positive electrode, and the yellow, cyan, magenta and black inks according to the present invention are continuously printed in sequence by the printing stages, respectively, thereby achieving process printing.

[0066] Hereinafter, although the present invention will be described in more details by way of examples, it is understood that the present invention should not be limited to such examples without departing from the technical idea of the present invention.

[0067] In the examples, a pH was measured with a glass electrode type hydrogenion densitometer manufactured by Denki Kagaku Keiki K.K.; a conductivity was measured with CONDUCTIVITY METER DS-12 manufactured by HORIBA; and a viscosity was measured with a B-type viscometer manufactured by TOKIMEC INC., respectively. Furthermore, the optical density of a printed matter was measured with X-Rite (trade mark) MODEL 408 manufactured by X-Rite.

Example 1

[0068] A black ink used as a starting ink was prepared from the following ingredients:

- Pigment sold under the trade mark "Carbon Black Monarch 120"	8.8% by weight
- Anionic dispersant aqueous solution sold under the trade mark "CLOSPERSE 2500"	0.75% by weight
- Anionic acrylamide polymer sold under the trade mark "ACCOSTRENGTH 86"	8.8% by weight
- Potassium chloride (soluble electrolyte)	8.8% by weight
- Disodium EDTA dihydrate (sequestering agent)	0.03% by weight
- Acetylene glycol based surfactant solution sold under the trade mark "Surfynol 104 PA"	0.1% by weight
- Biocidal agent sold under the trade mark "PARMETOL K-50"	0.1% by weight
- Water (liquid medium)	72.62% by weight
Total	100% by weight

[0069] The pigment was first dispersed into the water with the dispersant, using a sand mill, thereby obtaining a pigment dispersion. The polymer was then added to the resulting dispersion, followed by the addition of the potassium

chloride and the biocidal agent. The sequestering agent and "Surfynol 104 PA" available from Air Products Japan Inc. (an isopropyl alcohol solution of 2,4,7,9-tetramethyl-5-decyne-4,7-diol; effective ingredient: about 50% by weight) were admixed, then the solution was filtered and deaerated. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at 25 °C, and a viscosity of about 500 mPa·s at 30 °C.

[0070] The ink was used in an electrocoagulation printing apparatus of the type described in the aforementioned U. S. Patent No. 5,693,206, shown in Fig. 1. The printing apparatus comprises a positive electrode made of stainless steel, a device of cleaning the positive electrode with high pressure water containing a detergent, a device for forming micro-droplets of an oily substance at the surface of the positive electrode, an ink discharge unit, a plurality of negative electrodes being about 50 µm in diameter and spaced apart from the positive electrode by a fixed distance, a device for removing a non-coagulated ink from the surface of the positive electrode by means of a squeegee made of soft polyurethane and a pressure roller made of polyurethane. The ink, the detergent for use in the device for cleaning the positive electrode and the positive electrode cylinder were heated to 40 °C, and then, were used.

[0071] The optical density of the coagulated ink transferred onto the substrate was 1.3. No spotted background occurred during a continuous printing operation for about an hour. The optical density at a non-image portion of the printed matter was as low as 0.01. Thus, the good printed matter without any deterioration in quality caused by a spotted background was obtained.

Example 2

[0072] A cyan ink used as a starting ink was prepared from the following ingredients in the same manner as the black ink of

Example 1.

[0073]

- Copper-phthalocyanine based cyan pigment sold under the trade mark "Heliogen Blue D7072DD"	10.5% by weight
- Anionic dispersant aqueous solution sold under the trade mark "CLOSPERSE 2500"	4.2% by weight
- Anionic acrylamide polymer sold under the trade mark "ACCOSTRENGTH 86"	7% by weight
- Potassium chloride (soluble electrolyte)	8.4% by weight
- DTPA (sequestering agent)	0.03% by weight
- Acetylene glycol based surfactant solution sold under the trade mark "Surfynol 104 PA"	0.1% by weight
- Biocidal sold under the trade mark "PARMETOL K-50"	0.1% by weight
- Water (liquid medium)	<u>69.67% by weight</u>
Total	100% by weight

[0074] The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 105 mS/cm at 25 °C, and a viscosity of about 520 mPa·s at 30 °C.

[0075] The ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. No spotted background occurred during a continuous printing operation for about an hour. The optical density at a non-image portion of the printed matter was as low as 0.01. Thus, the good printed matter without any deterioration in quality caused by a spotted background was obtained.

Example 3

[0076] The magenta ink used as a starting ink was prepared from the same ingredients in the same manner as those

of Example 2 with the exception that the pigment was replaced by 10.5% by weight of azo based magenta pigment sold under the trade mark "Permanent Rubin F6B" and the sequestering agent was replaced by 0.03% by weight of EDTA out of the ingredients of the ink listed in Example 2.

[0077] The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 104 mS/cm at 25 °C, and a viscosity of about 520 mPa·s at 30 °C.

[0078] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. No spotted background occurred during a continuous printing operation for about an hour. The optical density at a non-image portion of the printed matter was as low as 0.01. Thus, the good printed matter without any deterioration in quality caused by a spotted background was obtained.

Example 4

[0079] The black ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 1 with the exception that the acetylene glycol based surfactant was replaced by 0.05% by weight of a compound expressed by the chemical formula (1) where R_1 and R_2 each were $\text{CH}_3\text{-CH}(\text{CH}_3)$ and $m+n$ was 2 and water was contained in an amount of 72.67% by weight out of the ingredients of the ink listed in Example 1.

[0080] The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at 25 °C, and a viscosity of about 510 mPa·s at 30 °C.

[0081] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. No spotted background occurred during a continuous printing operation for about an hour. The optical density at a non-image portion of the printed matter was as low as 0.01. Thus, the good printed matter without any deterioration in quality caused by a spotted background was obtained.

Example 5

[0082] The black ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 1 with the exception that "Surfynol 104 PA" as the acetylene glycol based surfactant was contained in an amount of 0.01% by weight and water was contained in an amount of 72.71% by weight out of the ingredients of the ink listed in Example 1. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at a temperature 25 °C, and a viscosity of about 490 mPa·s at 30 °C.

[0083] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. Unfavorable spotted background slightly occurred at a non-image portion of the printed matter in about 10 minutes after the beginning of the printing operation. However, the optical density of the portion with the spotted background was as low as 0.02. Thus, the printed matter with little deterioration in quality caused by the spotted background was obtained.

Example 6

[0084] The black ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 1 with the exception that "Surfynol 104 PA" as the acetylene glycol based surfactant was contained in an amount of 5% by weight and water was contained in an amount of 67.72% by weight out of the ingredients of the ink listed in Example 1. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at 25 °C, and a viscosity of about 530 mPa·s at 30 °C.

[0085] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was somewhat as low as 1.2. The optical density at a non-image portion of the printed matter was 0.02, which was slightly higher than those in the other examples. However, no spotted background occurred during a continuous printing operation for about an hour. Thus, the printed matter without any deterioration in quality caused by a spotted background was obtained.

Example 7

[0086] The black ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 1 with the exception that neither of the sequestering agent and the biocidal agent were contained and water was contained in an amount of 72.75% by weight out of the ingredients of the ink listed in Example 1. The ink thus

obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at 25 °C, and a viscosity of about 500 mPa·s at 30 °C.

[0087] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. No spotted background occurred during a continuous printing operation for about an hour. The optical density at a non-image portion of the printed matter was as low as 0.01. Thus, the good printed matter without any deterioration in quality caused by a spotted background was obtained. The viscosity of the ink was slightly increased in comparison with that in Example 1 when the printing time exceeded about 30 minutes.

Comparative Example 1

[0088] The black ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 1 with the exception that no acetylene glycol based surfactant was contained and water was contained in an amount of 72.72% by weight out of the ingredients of the ink listed in Example 1. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 112 mS/cm at 25 °C, and a viscosity of about 490 mPa·s at 30 °C.

[0089] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. Unfavorable spotted background occurred at a non-image portion of the printed matter in about 10 minutes after the beginning of the printing operation. The optical density of the portion with the spotted background was as high as 0.06. Thus, the quality of the printed matter was poor.

Comparative Example 2

[0090] The cyan ink used as a starting ink was prepared from the same ingredients in the same manner as those of Example 2 with the exception that no acetylene glycol based surfactant was contained and water was contained in an amount of 69.77% by weight out of the ingredients of the ink listed in Example 2. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 105 mS/cm at 25 °C, and a viscosity of about 490 mPa·s at 30 °C.

[0091] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. Unfavorable spotted background occurred at a non-image portion of the printed matter in about 10 minutes after the beginning of the printing operation. The optical density of the portion with the spotted background was as high as 0.06. Thus, the quality of the printed matter was poor.

Comparative Example 3

[0092] The magenta ink used as a starting ink was prepared from the same ingredients in the same method as those of Example 3 with the exception that no acetylene glycol based surfactant was contained and water was contained in an amount of 69.77% by weight out of the ingredients of the ink listed in Example 3. The ink thus obtained had a pH of about 4.1 at 25 °C, a conductivity of about 104 mS/cm at 25 °C, and a viscosity of about 490 mPa·s at 30 °C.

[0093] The obtained ink was used in the same electrocoagulation printing apparatus as in Example 1, and the quality of the resulting printed matter was evaluated in the same method as that in Example 1. The optical density of the coagulated ink transferred onto the substrate was 1.3. Unfavorable spotted background occurred at a non-image portion of the printed matter in about 10 minutes after the beginning of the printing operation. The optical density of the portion with the spotted background was as high as 0.06. Thus, the quality of the printed matter was poor.

Industrial applicability

[0094] As described above, the electrocoagulation printing ink according to the present invention is suitably used as the ink which can be readily removed from the surface of the cylindrical positive electrode even in the non-coagulated state.

[0095] Furthermore, the electrocoagulation printing ink according to the present invention is suitably used as the ink for forming the printed matter having the remarkably excellent quality, in which no spotted background occurs even if the printing time becomes long.

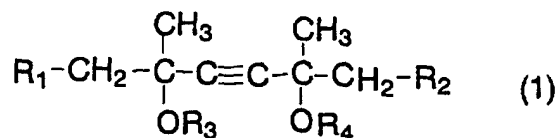
Claims

1. An electrocoagulation printing ink containing: an acetylene glycol based surfactant, an electrolytically coagulable

polymer, a coloring agent, a soluble electrolyte and a liquid medium.

2. The electrocoagulation printing ink according to claim 1, further containing a sequestering agent.

3. The electrocoagulation printing ink according to claim 1 or claim 2, wherein the acetylene glycol based surfactant is a nonionic acetylene glycol based surfactant expressed by a chemical formula (1),



where R_1 and R_2 each are CH_3-CH_2 or $\text{CH}_3-\text{CH}(\text{CH}_3)$; R_3 is $(\text{CH}_2\text{CH}_2\text{O})_m-\text{H}$; R_4 is $(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$; and $m+n$ is an integer ranging from 0 to 50.

4. The electrocoagulation printing ink according to claim 3, wherein the acetylene glycol based surfactant is 2,4,7,9-tetramethyl-5-decyne-4,7-diol.

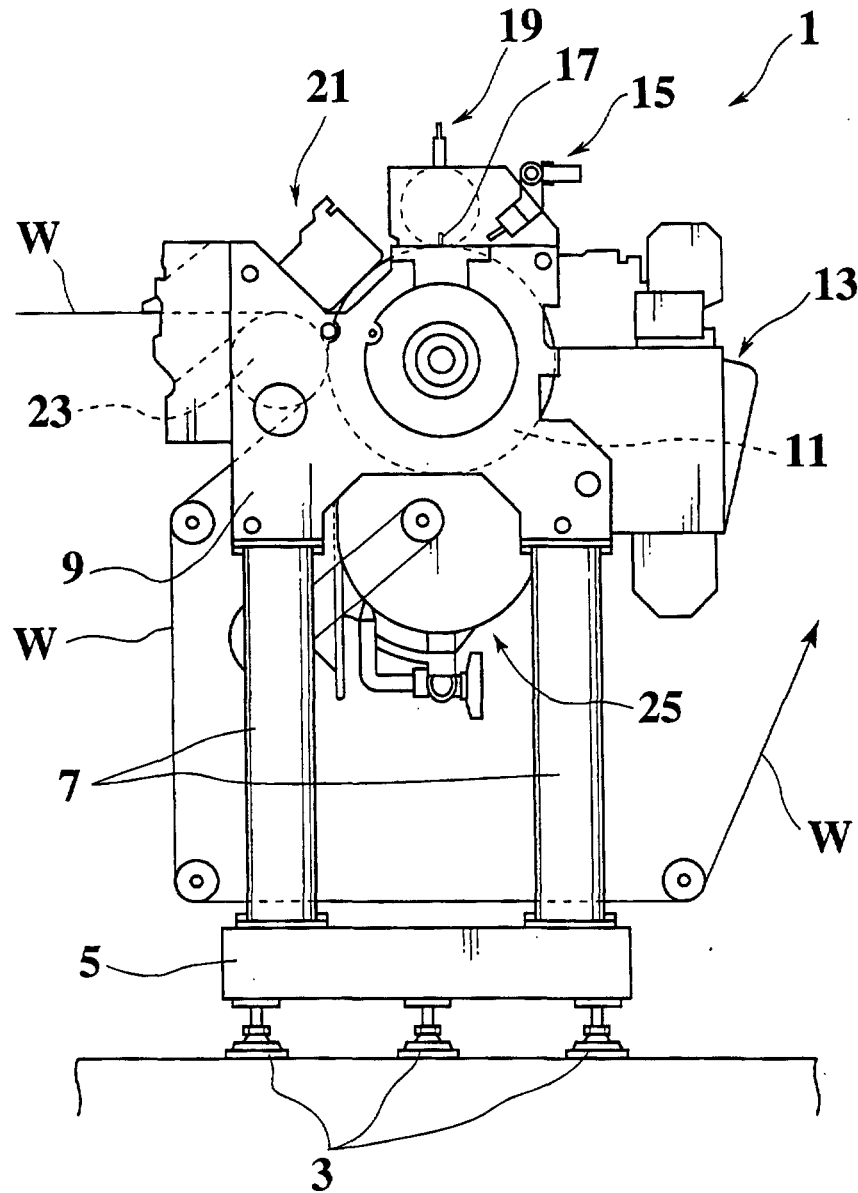
5. The electrocoagulation printing ink according to any one of claims 1, 2 and 4, wherein the acetylene glycol based surfactant is contained in an amount of 0.01 to 2% by weight based on the total weight of the ink.

6. The electrocoagulation printing ink according to claim 3, wherein the acetylene glycol based surfactant is contained in an amount of 0.01 to 2% by weight based on the total weight of the ink.

7. A printed matter printed with the electrocoagulation printing ink according to claim 1.

8. An electrocoagulation printing method using the electrocoagulation printing ink according to claim 1.

FIG.1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/06430

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ C09D11/02, 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.⁷ C09D11/00-11/20, B41M5/20

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

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.
EX	JP, 11-323227, A (Toyo Ink Manufacturing Co., Ltd.), 26 November, 1999 (26.11.99), Claims (Family: none)	1-8
Y	EP, 437318, A1 (Canon Inc.), 17 July, 1991 (17.07.91), Claims & JP, 4-222882, A & US, 5143546, A	1-8
Y	EP, 592774, A2 (Canon Inc.), 20 April, 1994 (20.04.94), Claims & JP, 6-25573, A & US, 5395434, A	1-8
Y	JP, 11-138984, A (Toyo Ink Manufacturing Co., Ltd.), 25 May, 1999 (25.05.99), Claims; Par. No. [0034], (Family: none)	1-8
A	WO, 96/18507, A1 (Toyo Ink Manufacturing Co., Ltd.), 20 June, 1996 (20.06.96), Claims & JP, 10-510575, A & EP, 802862, A1	1-8

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search
08 February, 2000 (08.02.00)

Date of mailing of the international search report
15 February, 2000 (15.02.00)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/06430

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	& US, 5750593, A	

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