

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 878 323 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

18.11.1998 Bulletin 1998/47

(51) Int Cl.⁶: **B41M 5/00**

(21) Application number: **98303758.1**

(22) Date of filing: **13.05.1998**

(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

• **Yoshizawa, Senichi**

Tomoe-machi, Shizuoka-shi, Shizuoka-ken (JP)

• **Onishi, Hiroyuki**

Suwa-shi, Nagano-ken (JP)

• **Itano, Masaaki**

Suwa-shi, Nagano-ken (JP)

• **Owatari, Akio**

Suwa-shi, Nagano-ken (JP)

(30) Priority: **13.05.1997 JP 137567/97**

(71) Applicants:

• **TOMOEGAWA PAPER CO. LTD.**

Chuo-ku, Tokyo 104 (JP)

• **SEIKO EPSON CORPORATION**

Shinjuku-ku Tokyo (JP)

(74) Representative: **Woods, Geoffrey Corlett**

J.A. KEMP & CO.

14 South Square

Gray's Inn

London WC1R 5LX (GB)

(72) Inventors:

• **Iwamoto, Kiyoshi**

Tomoe-machi, Shizuoka-shi, Shizuoka-ken (JP)

(54) **Inkjet recording sheet**

(57) An inkjet recording sheet comprising a substrate and, provided thereon, an ink receptor layer comprising:

(a) a polymer obtainable by polymerising a monomer composition comprising vinyl-polymerizable monomer containing a basic nitrogen atom; and
(b) 500 ppm or less of a polymerization inhibitor.

EP 0 878 323 A1

Description

Field of the Invention

5 The present invention relates to an inkjet recording sheet. More specifically, it relates to an inkjet recording sheet whose discoloration, which is caused with the passage of time, is prevented.

Prior Art of the Invention

10 Inkjet printers are widely used since they have features in clearness of colors, noiselessness and easiness in color expression. Inkjet printers use not a solvent-containing ink but a water-based ink for environmental safety. Generally, an ink contains, as main components, a colorant such as pigment or a dye, a water-based or water-soluble solvent, an additive, and the like. As an ink for an inkjet printer, there is used an ink which is not easily dried, in order to prevent the clogging of a nozzle caused by the drying of the ink.

15 A recording sheet for use with an inkjet printer is particularly required to have the capability of receiving water-based materials in order to cope with the above property of an ink. For this reason, there are generally used inkjet recording sheets having a structure in which an ink receptor layer capable of well receiving the ink is formed on a substrate.

20 There has been proposed an ink receptor layer which is formed by preparing, as a main component, a system containing a water-soluble polymer such as polyvinyl alcohol and a highly water-absorptive pigment such as silica and further incorporating other water-soluble polymer(s) and additives to the main component. The water-soluble polymer other than polyvinyl alcohol, etc., is used for improving the clearness of an image, the color formability of an ink or the fixing properties of an ink when the ink is used for recording with an inkjet printer. As the above "other" water-soluble polymer, a polymer containing a basic nitrogen atom has been proposed. The absorbability to an ink and the clearness

25 of an image are improved by incorporating the above polymer.

30 An inkjet recording sheet having a conventional ink receptor layer containing the above polymer containing a basic nitrogen atom has no practically sufficient storage durability and has a defect that it turns yellowish or reddish with the passage of time. In recent years, further, almost all inkjet printers tend to be used for full color printing. A recording sheet for full color printing is required to have a high whiteness, and the above defect particularly remains to solve.

Summary of the Invention

It is an object of the present invention to provide an inkjet recording sheet whose discoloration, which is caused with the passage of time, is prevented.

35 According to the present invention, there is provided an inkjet recording sheet comprising a substrate and an ink receptor layer formed on the substrate, the ink receptor layer containing a polymer obtained from a monomer component containing at least vinyl-polymerizable monomer containing a basic nitrogen atom, the ink receptor layer containing a polymerization inhibitor in a decreased amount of 500 ppm or less, preferably 300 ppm or less, particularly preferably 200 ppm or less.

Detailed Description of the Invention

40 The substrate for use in the inkjet recording sheet of the present invention includes non-transparent substrates such as paper, cloth and non-woven fabric, films obtained from plastics such as polyethylene terephthalate, diacetate cellulose, triacetate cellulose, an acrylic polymer, Cellophane, celluloid, polyvinyl chloride, polycarbonate and polyimide, a wooden plate and a glass plate. The substrate is selected as required depending upon an object in recording, use of a recorded image or adhesion to an ink receptor layer.

45 In the present invention, the ink receptor layer contains a polymer obtained from a monomer component containing at least a vinyl-polymerizable monomer containing a basic nitrogen atom. The vinyl-polymerizable monomer containing a basic nitrogen atom includes N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, acrylamide, diacetylacrylamide, N-methylolacrylamide, N-vinylpyridine, N-vinylpyrrolidone, N-vinylloxazoline, N-vinylloxazolidone, N-vinylformamide, N-vinylamine, and quaternary ammonium salts obtained from these. Of these, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N-vinylamine and quaternary ammonium salts of these are preferred. In the present invention, since a polymer obtained from a monomer component containing at least

50 one monomer selected from the above N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N-vinylamine or quaternary ammonium salts of these gives an inkjet recording sheet which is excellent in absorption of an ink and the clearness of a color image.

55 The present invention uses a homopolymer or a copolymer obtained from the above vinyl-polymerizable monomer

containing a basic nitrogen atom. The above copolymer is obtained from a combination of the above monomers or from at least one of the above monomers and other vinyl monomer. The "other" vinyl monomer includes (meth)acrylic acid and ester derivatives thereof, and also includes vinyl alcohol, vinyl acetate, styrene and derivatives of these.

In the present invention, there may be incorporated a resin other than the polymer obtained from the vinyl-polymerizable monomer containing a basic nitrogen atom.

The above "other" resin includes an acrylic resin, a polyester resin, a polyurethane resin, a styrenebutadiene copolymer resin, an acrylonitrile-butadiene copolymer resin, a polyvinyl alcohol resin, a water-soluble polyvinyl acetal resin, a polyvinyl butyral resin, other vinyl resin, an amide resin, oxidized starch, casein, polyethylene oxide, a silicone resin, a rosin-modified maleic acid resin, a rosin-modified phenolic resin, an alkyd resin, and a coumarone-indene resin. Of these resin, a water-soluble resin such as a polyvinyl alcohol resin or a water-soluble polyvinyl acetal resin is preferred in view of the absorptivity to an ink, the drying properties of an ink and the clearness of an image.

In the present invention, it has been found that the discoloration can be prevented by decreasing the content of a polymerization inhibitor which is generally contained in a polymer obtained from a monomer component containing a vinyl-polymerizable monomer containing a basic nitrogen atom. In the present invention, the method of decreasing the content of a polymerization inhibitor in the ink receptor layer is not specially limited. For example, the content of a polymerization inhibitor can be decreased by one of the following methods.

① A method in which the amount of a polymerization inhibitor to be added to the vinyl-polymerizable monomer containing a basic nitrogen atom is decreased, or no polymerization inhibitor is added, and a monomer is polymerized immediately, or within a short period of time, after it is produced, to produce a polymer. ② A method in which a polymer obtained by the polymerization is purified or washed to remove a polymerization inhibitor. ③ A method in which a group containing a basic nitrogen atom is later introduced into a polymer containing no basic nitrogen atom.

The polymerization inhibitor includes diphenylpicrylhydrazyl (DPPH), di-p-fluorophenylamine, tri-p-nitrophenylmethyl, benzoquinone, chloranil, p-tert-butyl catechol, hydroquinone m-nitrobenzene, nitrobenzene and p-phenyldiamine.

In the present invention, a pigment may be incorporated into the ink receptor layer. The pigment can be selected from conventional fillers and organic or inorganic pigments such as silica, clay, mica, swelling mica, talc, kaolin, diatomaceous earth, calcium carbonate, barium sulfate, aluminum silicate, synthetic zeolite, alumina, zinc oxide, lithopone and satin white. The average particle diameter (volume average particle diameter measured by coulter counter method) is preferably 1 to 25 μm , particularly preferably 5 to 25 μm . When the above particle diameter is less than 1 μm , the absorptivity to an ink may be impaired. When the above particle diameter exceeds 25 μm , the pigment may fall off or an image may be roughened.

In the present invention, the ink receptor layer preferably contains 5 to 100 % by weight of a polymer obtained from a component containing vinyl-polymerizable monomer containing a basic nitrogen atom. When the above pigment is contained in combination, the ink receptor layer preferably contains 5 to 60 % by weight of the above polymer. The content of the pigment in the ink receptor layer is preferably 40 to 95 % by weight, particularly preferably 60 to 90 % by weight. The ink receptor layer containing the above polymer and the pigment in the above amount ratio particularly attains excellent absorptivity to an ink and excellent clearness of an image.

The ink receptor layer may contain other additive for improving water resistance and preventing bleeding. The above "other" additive includes a melamine formaldehyde resin, a urea formaldehyde resin, glyoxazole and zirconium carbonate ammonium. For further improving the productivity, recording properties or storage stability of an inkjet recording sheet, the ink receptor layer may contain various additives such as a dispersing agent, a fluorescent dye, a pH adjuster, an anti-foaming agent, a lubricant and an antiseptic.

The ink receptor layer is formed on a substrate by dissolving or dispersing materials for forming the ink receptor layer in water or a proper solvent to obtain a coating solution or dispersion and applying the coating solution or dispersion onto the substrate according to a proper application method such as a roll coating method, a blade coating method, a gravure coating method, comma coating method, a rod bar coating method, an air knife coating method or a dye coating method. Further, the above coating solution or dispersion may be laminated on the substrate by a hot melt coating method or a laminate coating method. The ink receptor layer may have a laminate structure of at least two layers.

The application amount of the ink receptor layer is preferably 5 to 30 g/m^2 , particularly preferably 10 to 20 g/m^2 . When the application amount exceeds 30 g/m^2 , the ink receptor layer is not improved in properties any further. When the application amount is less than 5 g/m^2 , the absorptivity to an ink may be insufficient.

The inkjet recording sheet of the present invention may be provided with added value by imparting its surface with a gloss. The gloss may be imparted by a method in which the ink receptor layer is formed according to a cast coating method, a method in which the ink receptor layer is surface treated with a calender or a method in which a glossy layer is laminated on the ink receptor layer. For obtaining an excellent gloss appearance, the layer imparted with gloss preferably has a glossiness of at least 10 according to a 60 degree surface glossiness test. The glossy layer preferably contains, as main components, the same resin and the same pigment as those used for the ink receptor layer, since the glossy layer is improved in adhesion to the ink receptor layer. The glossy layer is produced and laminated, for example, by a method in which a coating composition for forming the glossy layer is applied to a substrate film which

EP 0 878 323 A1

shows poor adhesion to materials for forming the glossy layer, such as a polyolefin resin film, an ethylene tetrafluoride resin film or a film treated with a peeling silicone, then, the resultant laminate is stacked on the ink receptor layer, drying the stacked product and peeling the substrate film.

In the glossy layer, the amount ratio of a binder resin and a pigment is as follows. The amount of the binder resin based on the pigment is preferably 5 to 50 % by weight, particularly preferably 5 to 30 % by weight. For imparting an excellent gloss by means of the glossy layer without impairing the function of the ink receptor layer, the thickness of the glossy layer is preferably 5 to 12 μm , particularly preferably 8 to 10 μm .

Examples

The present invention will be explained with reference to Examples hereinafter. In Examples, "part" and "%" stand for "part by weight" and "% by weight" unless otherwise specified.

Preparation Examples 1 - 7

Polymers were prepared from monomers shown in the following Table 1 according to a solution polymerization method.

Table 1

PEx.	Monomer containing basic nitrogen atom (A)	Comonomer (B)	Copolymerization ratio A/B	Polymerization inhibitor	Amount of polymerization inhibitor
1	Dimethylaminoethyl methacrylate	Acrylic acid	95/5	Hydroquinone monomethyl ether	50 ppm
2	Quaternary ammonium salt from dimethylaminoethyl methacrylate	Styrene	90/10	Hydroquinone monomethyl ether	50 ppm
3	Polyvinylamine	Nil	100/0	Nil	Nil
4	Polyvinylamine	Acrylic acid	95/5	Nil	Nil
5	Dimethylaminoethyl methacrylate	Acrylic acid	95/5	Hydroquinone monomethyl ether	250 ppm
6	Dimethylaminoethyl methacrylate	Acrylic acid	95/5	Hydroquinone monomethyl ether	500 ppm
7	Dimethylaminoethyl methacrylate	Acrylic acid	95/5	Hydroquinone monomethyl ether	1,000 ppm

Notes: PEx. = Preparation Example

In Preparation Example 3, the polymer was prepared by hydrolyzing a polyvinylformamide aqueous solution with sodium hydroxide.

In Preparation Example 4, the polymer was prepared by hydrolyzing a polyvinylformamide/acrylic acid (= 95/5) copolymer aqueous solution with sodium hydroxide.

Examples 1 - 7

Coating composition for ink receptor layer	
Polymer obtained in one of Preparation Examples 1 to 7 (solid content 37 %)	250 parts
Silica ("CARPLEX BS304F", supplied by Shionogi Pharmaceutical)	180 parts
Water	850 parts

The above coating composition was applied to a corona-discharge-treated 100 μm thick polyester film so as to form a coating having a dry weight of 15 g/m^2 and dried to form an ink receptor layer. In this manner, inkjet recording

sheets of the present invention were obtained.

Comparative Example 1

5 An inkjet recording sheet was obtained in the same manner as in Example 1 except that the polymer contained in the coating composition for forming the ink receptor layer was replaced with a dimethylaminoethyl methacrylate/acrylic acid (= 95/5) copolymer prepared from a commercially available dimethylaminoethyl methacrylate (containing 2,000 ppm of hydroquinone monomethyl ether) and acrylic acid.

10 Comparative Example 2

An inkjet recording sheet was obtained in the same manner as in Example 1 except that the polymer contained in the coating composition for forming the ink receptor layer was replaced with a polyvinyl alcohol ("GOHSENOL T-330, 10 % aqueous solution, supplied by Nippon Gosei Kagaku K.K.).

15 The inkjet recording sheets obtained in Examples 1 to 7 and Comparative Examples 1 and 2 were cut to a size of A4 (210 mm' x 297 mm), and color printing was effected on each sheet with an inkjet printer ("MJ-5000C" supplied by Seiko-Epson) using an inkjet printing ink ("MJIC2C" supplied by Seiko-Epson). The resultant printed products were evaluated for various properties or performances as follows. Table 2 shows the results.

20 (1) Performance of prevention of discoloration

A sheet was allowed to stand indoors for 7 days, and then evaluated for a degree of discoloration.

- 25 A: Almost no discoloration.
 B: Intermediate state between A and C.
 C: Turned yellowish or reddish.

(2) Color formation

30 A printed product was visually evaluated for clearness of an image and color formability of the ink.

- A: Excellent image.
 B: Intermediate state between A and C.
 C: Poor image.

35 (3) Fixing properties

A sheet of paper was stacked on a printed product immediately after it was obtained, and a finger was rubbed against the paper to visually evaluate the transfer of the ink to the paper.

- 40 A: Almost no ink was transferred to the paper.
 B: Intermediate state between A and C.
 C: The ink was saliently transferred to the paper.

45

Table 2

	Polymerization inhibitor	Prevention of discoloration	Color formability	Fixing properties
Ex. 1	17	A	A	A
Ex. 2	17	A	A	A
Ex. 3	0	A	A	A
Ex. 4	0	A	A	A
CEx. 1	680	C	A	A
CEx. 2	0	A	C	C
Ex. 5	85	A	A	A

50

55

Table 2 (continued)

	Polymerization inhibitor	Prevention of discoloration	Color formability	Fixing properties
5 Ex. 6	170	A	A	A
Ex. 7	340	B	A	A
Notes: Ex. = Example, CEx. = Comparative Example				

10 Values in the column of "Polymerization inhibitor" represent contents (ppm) of polymerization inhibitors in ink receptor layers.

The results in Table 2 clearly show that the inkjet recording sheets of the present invention are excellent in performance of prevention of discoloration and color formability, and they are also excellent in fixing properties such as absorptivity to the ink.

15 As explained above, according to the present invention, there is provided an inkjet recording sheet which is excellent in color formability and fixing properties required of inkjet recording sheets and which is also excellent in the performance of prevention of discoloration.

20 Claims

1. An inkjet recording sheet comprising a substrate and, provided thereon, an ink receptor layer comprising:

(a) a polymer obtainable by polymerising a monomer composition comprising a vinyl-polymerizable monomer containing a basic nitrogen atom; and

25 (b) 500 ppm or less of a polymerization inhibitor.

2. A sheet according to claim 1, wherein the ink receptor layer contains from 5 to 100% by weight of the vinyl-polymerizable monomer.

30 3. A sheet according to claim 1 or 2, wherein the ink receptor layer further comprises a pigment in an amount of from 40 to 95% by weight.

35 4. A sheet according to any one of the preceding claims, wherein the vinyl-polymerizable monomer is selected from dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, N-vinylamine and quaternary ammonium salts thereof.

5. A sheet according to any one of the preceding claims, wherein the polymerization inhibitor is present in the ink receptor layer in an amount of 300 ppm or less.

40 6. A sheet according to any one of the preceding claims, wherein the ink receptor layer further comprises a polyvinyl alcohol resin or a water-soluble polyvinyl acetal resin.

7. A sheet according to any one of the preceding claims, wherein the monomer composition further comprises (meth) acrylic acid or an ester thereof, or vinyl alcohol, vinyl acetate, styrene or a derivative thereof.

45 8. A sheet according to any one of the preceding claims, wherein the ink receptor layer is provided on the substrate in an amount of from 5 to 30 g/m².

50 9. A process for preparing a printed image, which process comprises applying a water based ink to a recording sheet according to any one of the preceding claims using an inkjet printer.

10. A printed image obtainable by a process according to claim 9.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 3758

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 627 324 A (MITSUBISHI PAPER MILLS LTD) 7 December 1994 * page 3, line 6 - page 6, line 17 * * page 9, line 44 - page 10, line 5 * * examples * ---	1-10	B41M5/00
P,A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 011, 28 November 1997 & JP 09 183928 A (NIPPON KAYAKU CO LTD), 15 July 1997 * abstract * -----	1,9,10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 September 1998	Examiner Markham, R
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (P04C01)