

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

Publication number:

0 608 799 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **94100953.2**

(51) Int. Cl.⁵: **B41M 5/00**

(22) Date of filing: **24.01.94**

(30) Priority: **25.01.93 JP 10004/93**

(43) Date of publication of application:
03.08.94 Bulletin 94/31

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE**

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(54) **Recording paper and ink-jet recording process making use of the same.**

(57) Disclosed herein is recording paper suitable for use in ink-jet recording systems making use of an ink containing a nitrogen compound, comprising neutral or alkaline paper as a base, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink thereon, in the interior thereof.

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BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to so-called plain paper to which a special coating is not applied, and particularly to recording paper comprising neutral or alkaline paper as a base with an excellent long-term shelf stability and permitting the formation of clear images.

The present invention also relates to an ink-jet recording process making use of widely-usable recording paper which exhibits excellent properties even as toner-transfer paper suitable for use in electrophotographic recording systems and permits the formation of clear images even in ink-jet recording.

This invention further relates to an ink-jet recording process which causes no clogging in nozzles of an ink-jet recording head and permits recording excellent in stability.

The term "neutral or alkaline paper" used in the present invention means a paper which is made so as to make the water extracted pH not less than 6 and without using aluminium sulfate as possible.

Related Background Art

Ink-jet recording systems have attracted attention because of ready attainment of high-speed, high-density and full-color recording. Such exclusive coated paper sheets as disclosed in, for example, Japanese Patent Application Laid-Open Nos. 59-35977 and 1-135682 have been used in such ink-jet recording systems.

Meanwhile, in the fields of black-and-white recording and business color recording, there has been demand for development of recording paper low in price and widely usable, in particular, recording paper usable in common as toner-transfer paper (paper for PPC) for copying machines and the like making use of an electrophotographic recording system, which are in common use in offices at present.

Problems involved in ink-jet recording making use of paper for PPC are the following two points:

(1) ink absorptivity is poor, so that when a great amount of an ink is applied to the paper, the drying and fixing of the ink are delayed (if an object comes into contact with the recorded surface in the state that the ink is neither fixed nor dried, the image formed is impaired); and

(2) an ink spreads along fibers of the paper at the time the ink is absorbed in a paper layer, so that feathering of dots occurs to a great extent, and the peripheries of the dots hence become jagged and blurred, resulting in failure of the provision of clear characters and images.

Meanwhile, in recent years, occasions to use neutral or alkaline paper in place of the conventional acid paper have increased due to problems of the shelf stability of paper and the like. Toner-transfer paper sheets excellent in electrophotographic recordability composed of neutral or alkaline paper are disclosed in Japanese Patent Application Laid-Open Nos. 51-13244 and 59-162561.

In ink-jet recording making use of these neutral or alkaline paper sheets for PPC, a phenomenon called "bronzing" in which the hue of a black recorded area locks brownish has presented itself, and a new problem has hence been offered.

Ink-jet ink is composed principally of a recording agent (dye), water as a solvent and a water-soluble, high-boiling organic solvent (polyhydric alcohol or the like) for preventing it from clogging due to its drying on the tip of a nozzle of an ink-jet recording head. One of methods for improving the above-described problems in recording making use of plain paper (paper for PPC) includes a method of designing an ink, in which a high-boiling organic solvent in the ink is decreased, whereby the wettability of the ink to a size in a paper layer is made poor so as to suppress the penetration of the ink into the paper layer, facilitate the fixing of the ink owing to evaporation of the solvent on a recording surface, and form dots having adequate and even feathering.

However, the reduction in the amount of the organic solvent results in worsened clogging of nozzle. Accordingly, it is common to add a solubilizer for the dye to the ink. Dyes used in ink-jet recording are generally acid dyes or direct dyes having an acid functional group. The ink generally includes, as a solubilizer, a nitrogen compound such as ammonia (ammonium ion), urea or a derivative thereof, aminoalcohol, alkylamine, or amino acid. The nitrogen compound also acts as a fixing agent upon fixing of the dye in the ink to pulp fibers of the paper.

In the ink-jet recording process making use of the above-described ink, however, the phenomenon of bronzing becomes more marked, which offers a problem.

In ink-jet recording methods making use of neutral or alkaline paper in particular, as described above, there has not yet been obtained any process, which can satisfy all the above-mentioned recordability requirements.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide novel recording paper which is excellent in ability to fix and dry inks, gives adequate and even feathering to dots and hence permits the formation of clear characters and images, and particularly causes no bronzing, and an ink-jet recording process making use of such paper.

Another object of the present invention is to provide an ink-jet recording process making use of recording paper usable in both electrophotographic recording and ink-jet recording, said process being suitable for use in black-and-white recording and business color recording, which need not use special exclusive paper (make use of general-purpose paper).

Such objects can be achieved by the present invention described below.

According to the present invention, there is thus provided recording paper suitable for use in ink-jet recording systems making use of an ink containing a nitrogen compound, comprising neutral or alkaline paper as a base, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink thereon, in the interior thereof.

According to the present invention, there is also provided an ink-jet recording process comprising applying an ink containing a dye, a low-boiling solvent and a nonvolatile solvent to neutral or alkaline paper to conduct recording, wherein ink droplets are applied to a recording surface of the neutral paper so as to evaporate the low-boiling solvent in the ink on the recording surface, and then to cause the nonvolatile solvent to penetrate into the paper while preventing the orientation of the dye.

According to the present invention, there is further provided an ink-jet recording process comprising conducting recording on neutral or alkaline paper with an ink containing a nitrogen compound as a solubilizer for a dye, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink thereon, in the interior thereof.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will hereinafter be described in more detail by the preferred embodiments of this invention. The recording paper used in the present invention is made by using chemical pulp typified by LBKP, NBKP and/or the like, a size and a filler as main components, and optionally other auxiliaries for paper making in accordance with the method known *per se* in the art. As the pulp material to be used, mechanical pulp and/or regenerated pulp from waste paper may be used in combination with the chemical pulp. Alternatively, they may be used as a main component.

Example of the size include rosin sizes, alkylketene dimers, alkenylsuccinic anhydrides, petroleum resin sizes, epichlorohydrin, cationic starch, acrylamide and the like.

The recording paper according to the present invention is adjusted to a water extracted pH of 6 or higher, preferably 7 or higher.

The water extracted pH is determined by measuring the pH of an extract obtained by immersing about 1.0 g of a test piece prescribed in JIS-P-8133 in 70 ml of distilled water in accordance with JIS-Z-8802. If the pH does not reach the above limit, a problem is offered from the viewpoint of the long-term shelf stability of the paper itself, and moreover the coloring ability of dyes may not be sufficiently exhibited on the paper in some cases.

If the Stöckigt sizing degree of the recording paper thus adjusted is too low, ink droplets applied to such paper feather to a too great extent, and difficulties are hence encountered on the formation of clear images and characters. On the contrary, if the sizing degree is too high, an ink applied to such paper is not absorbed in the paper layer long afterward, so that the ability to fix and dry the ink applied is deteriorated. It is hence preferable that the Stöckigt sizing degree be within a range of from 16 to 40 seconds.

The first feature of the present invention is that the recording surface of the recording paper formed in the above-described manner contains a penetration-retarding agent for inks. The penetration of the ink applied to the recording surface of the paper according to the present invention into the paper layer is slowed down by about 0.01 second to several seconds owing to the action of the penetration-retarding agent. In the meantime, most of a low-boiling solvent such as water is evaporated on the surface of the paper, and a nonvolatile solvent is then caused to penetrate into the paper layer.

Owing to this effect, the ink does not spread to a greater degree than the recording needs. In addition, the dye remains near the recording surface, so that dots high in contrast are formed.

Preferred materials for the penetration-retarding agent include casein, starch, cellulose derivatives such as carboxymethyl cellulose and hydroxyethyl cellulose, hydrophilic resins swellable in inks, such as polyvinyl alcohol, polyvinyl pyrrolidone, sodium polyacrylate and polyacrylamide, SBR latices, acrylic emulsions, resins having a hydrophilic moiety and a hydrophobic moiety in their molecules, such as styrene/maleic acid copolymers and styrene/acrylic acid copolymers, substances having water repellency, such as silicone oil, paraffin wax and fluorine compounds, the above-described sizes, and the like.

These materials are applied to the recording surface in a proportion of about 0.1 to 3 g/m².

The recording paper retains the penetration-retarding effect so long as such materials are contained within the above range. In addition, the remaining ink which is a residue after evaporation including the nonvolatile solvent penetrates into the paper layer to be absorbed therein, so that the ink-fixing ability is not lowered to an extreme extent.

The second feature of the present invention is that a substance adsorbing ammonia or ammonium ions generated from the nitrogen compound in the ink thereon is contained in the paper layer.

Examples of such a substance include the following compounds:

Finely powdered silicic acid; synthetic aluminum silicate; diatomaceous earth; kaolin minerals including kaolin, such as kaolinite, halloysite, nacrite and dickite; fillers such as pyrophyllite, sericite, titanium dioxide, bentonite and activated clay; polymers, for example, homopolymers of monomers such as acrylic acid or methacrylic acid or copolymers of such a monomer with other general monomers, homopolymers of α, β -unsaturated acids such as maleic acid and methacrylic acid or copolymers of such a monomer with other general monomers, polymers containing a sulfonic group, and acid cellulose derivatives modified with an ester of a polycarboxylic acid with a polyhydric alcohol or a polycarboxylic acid, and their salts with alkali metals such as sodium and potassium; and surfactants such as sodium lauryl sulfate, sodium cetyl sulfate, sodium polyoxyethylene lauryl ether sulfate, sodium lauryl phosphate, sodium polyoxyethylene lauryl ether phosphate and salts of alkylbenzenesulfonic acids, alkylsulfosuccinic acids and the like.

Of these, kaolin minerals and synthetic aluminum silicate are particularly preferred from the viewpoint of the prevention of the bronzing phenomenon.

In order to form dots sharp and even in edge, adequate in feathering on the paper surface and high in color depth (to form images good in print quality), as described above, it is desired as the features of both ink and paper that ink droplets applied to the recording surface be not absorbed in the paper layer in a moment, but absorbed therein after the evaporation of the solvent in the ink is completed to some extent on the paper surface.

Meanwhile, according to the finding of the present inventors, the bronzing is a phenomenon that in particular, black printed areas look brownish because a part of a dye in an ink aggregates in an orientated form so as to deposit on the paper surface without being absorbed in the paper layer. Accordingly, to make the print quality good by the above process is a problem contrary to the prevention against the occurrence of bronzing.

In addition, the problems of bronzing is marked in the case where inks containing a nitrogen compound such as urea are used. The reason for this is believed to be attributable to the fact that ammonia or ammonium ions generated from the nitrogen compound facilitate the orientation and aggregation of the dye in the course of the evaporation of the solvent on the paper surface, so that the deposition of the dye from the residual solvent for the ink is accelerated.

The reason why the bronzing markedly occurs in neutral or alkaline paper having a water extracted pH not lower than 7 is presumed to be the same as described above.

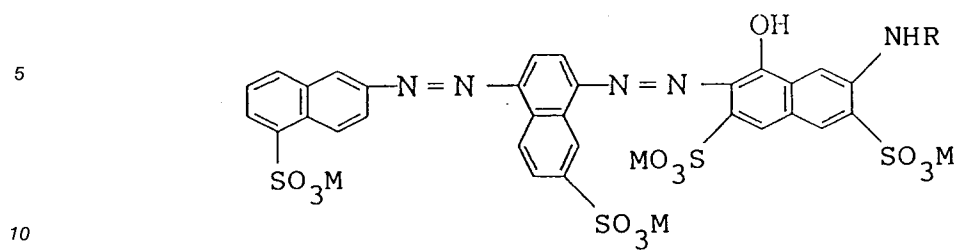
According to the present invention, since the paper contains the substance adsorbing NH₃ or NH₄⁺ ions generated from the nitrogen compound in the ink thereon, ink-jet recorded images good in print quality and free of any bronzing can be provided while maintaining advantages brought about by the recording method making use of an ink containing a nitrogen compound and neutral paper.

Further, since the recording paper according to the present invention does not very differ from the conventional neutral paper for PPC in surface profile and physical properties other than the recordability, it may be applied to both toner-transfer paper for electrophotographic recording and ink-jet recording paper.

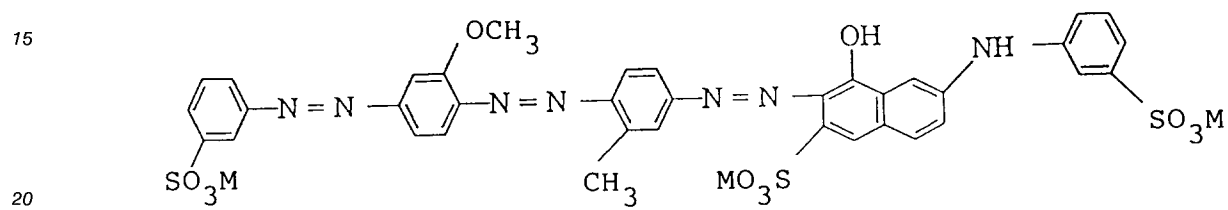
As described above, the ink used in the ink-jet recording process according to the present invention comprises water as a main component and contains a nonvolatile organic solvent such as a polyhydric alcohol, a low-boiling solvent such as a monohydric alcohol, a dye as a recording agent and a nitrogen compound as a solubilizer for the dye, and optionally other additives.

Any conventionally-known acid dyes and direct dyes may be employed as the dye to be used. However, particularly preferred are the following black dyes:

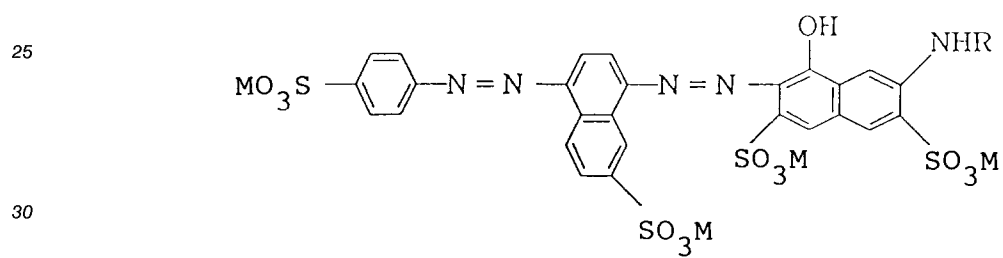
(1)



(2)



(3)



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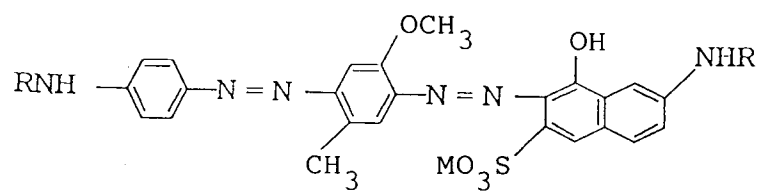
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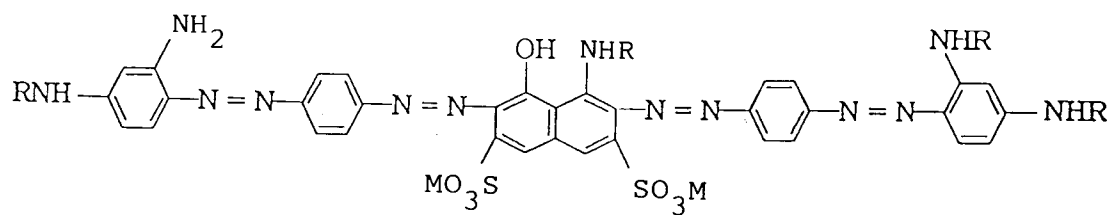
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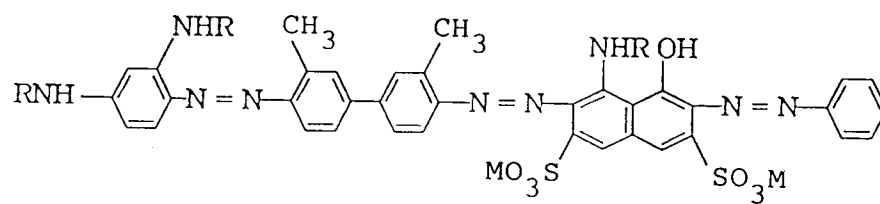
(4)



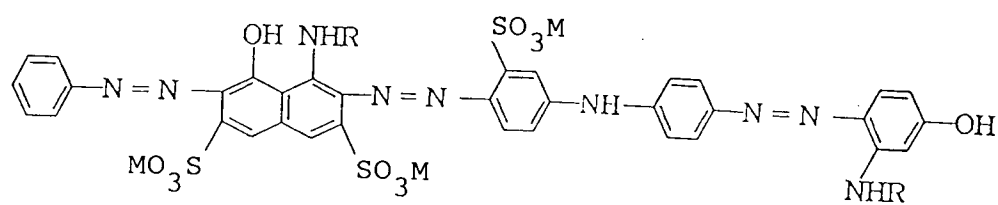
(5)



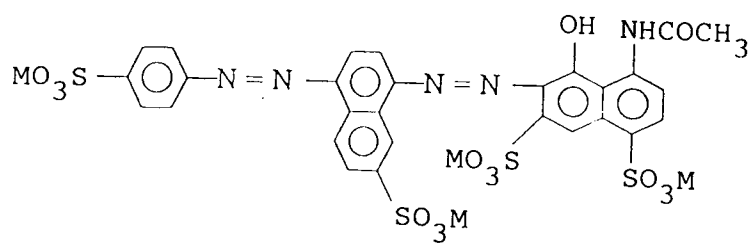
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(7)

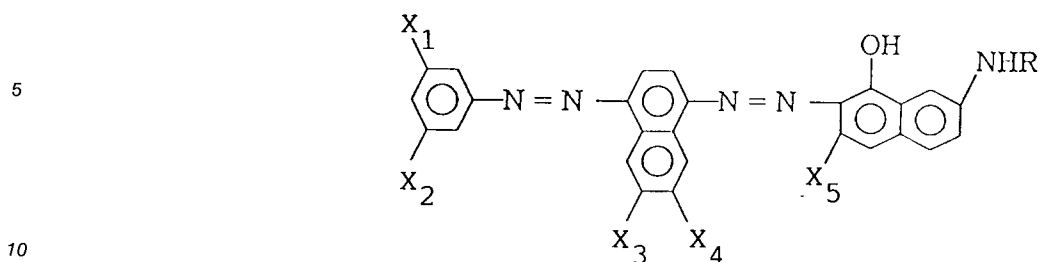


(8)



and

(9)



In the above dyes, M is Na or Li, R is H or an alkyl group, X₁ through X₅ are individually H, SO₃ Y₁ or COOY₂ where Y₁ and Y₂ are individually Na, Li, K or NH₄.

15 Ink-jet recording systems to which the processes of the present invention can be applied may include any conventionally-known ink-jet recording systems in which minute droplets of an ink are ejected from a nozzle by using various principles of drive to conduct recording.

Among others, the present invention may be particularly effectively used in an ink-jet recording system according to the method described in Japanese Patent Application Laid-Open No. 54-59936, in which an ink undergoes a rapid volumetric change by an action of thermal energy applied to the ink, so that the ink is ejected through an nozzle by the working force generated by this change of state.

The present invention will hereinafter be described in more detail by the following examples.

(Preparation of recording paper)

25 A recording base paper web having a basis weight of 70 g/m² and a Stöckigt sizing degree of 23 seconds was made in accordance with the method known per se in the art by mixing 90 parts of LBKP and 10 parts of NBKP as ray pulp, beating the mixture and then incorporating 10 parts of kaolin (product of Tsuchiya Kaolin Ind., Ltd.), 0.2 part of alkenylsuccinic anhydride and 0.5 part of cationic starch into the mixture. A 2 % aqueous solution of a penetration-retarding agent having the following composition was prepared to apply it to this base paper web at a rate of 1 g/m² by an air spray coating, thereby preparing Recording Paper A according to the present invention.

(Composition of penetration-retarding agent)

Oxidized starch (MS-3800, product of Nihon Shokuhin Kako Co., Ltd.)	95 parts
Styrene/maleic acid copolymer (Oxylac, product of Nippon Shokubai Kagaku Kogyo Co., Ltd.)	5 parts

40 A recording base paper web having a basis weight of 70 g/m² and a Stöckigt sizing degree of 27 seconds was then made in the same manner as in Recording Paper A except that alkenylsuccinic anhydride and kaolin in the preparation of Recording Paper A were changed in an alkylketene dimer and synthetic aluminum silicate (product of Kyowa Chemical Industry Co., Ltd.), respectively.

45 Recording Paper B was prepared in the same manner as in Recording Paper A except that a penetration-retarding agent having the following composition was used for this base paper web.

(Composition of Penetration-retarding agent)

Polyvinyl alcohol (product of Kuraray Co., Ltd.)	100 parts
Polyoxyethylene laurylsulfuric acid ether	0.1 part

55 A recording base paper web having a basis weight of 90 g/m² and a Stöckigt sizing degree of 33 seconds was further made in the same manner as in Recording Paper A except that alkenylsuccinic anhydride and kaolin in the preparation of Recording Paper A were changed to an alkylketene dimer, and finely powdered silica (Nipsil, product of Nippon Silica Industrial Co., Ltd.) and calcium carbonate (Escalon,

product of Sankyo Seifun K.K.) respectively.

Recording Paper C was prepared in the same manner as in Recording Paper A except that a penetration-retarding agent having the following composition was used for this base paper web.

5 (Composition of penetration-retarding agent)

Alkylketene dimer	100 parts
Polyoxyethylene laurylsulfuric acid ether	0.2 part

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A recording base paper web having a basis weight of 70 g/m² and a Stöckigt sizing degree of 27 seconds was further made in the same manner as in Recording Paper A except that alkenylsuccinic anhydride in the preparation of Recording Paper A was changed to neutral rosin size (Sizepine NT, product of Arakawa Chemical Industries, Ltd.)

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The same coating formulation as that used in Recording Paper A was used to prepare Recording Paper D in the same manner as in Recording Paper A.

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Recording Paper E was further prepared in the same manner as in Recording Paper A except that alkenylsuccinic anhydride and kaolin in the preparation of Recording Paper A were changed to an alkylketene dimer and calcium carbonate (Escalon, product of Sankyo Seifun K.K.), respectively, and the composition of the penetration-retarding agent was changed to 100 parts of oxidized starch alone.

The base paper web of Recording Paper E before the application of oxidized starch was provided as Recording Paper F.

25 (Composition of ink)

Ink a:

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Dye [a mixture of the specifically exemplified compounds (1), (2) and (3), wherein the counter ions are Li for (1) and (2), and Na for (3)]	3 parts
Diethylene glycol	5 parts
Ethanol	5 parts
Urea	5 parts
Water	82 parts

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Ink b:

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The composition was the same as that in Ink a except that the dye in Ink a was replaced by the compound (3) alone.

Ink c:

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The composition was the same as that in Ink a except that the dye in Ink a was replaced by a mixture of the compounds (1) and (2), and urea was changed to monoethanolamine.

Ink d:

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The composition was the same as that in Ink a except that the dye in Ink a was replaced by the compound (5) alone.

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Using recording paper and ink according to the following combinations, recording was conducted by a recording apparatus equipped with a recording head of an ink-jet system that ink droplets are ejected by the action of heat, said head having recording nozzles in a proportion of 14 nozzles per mm, thereby evaluating recordability. The results are shown in Table 1.

(Evaluation items)

(1) Print quality:

5 A straight line having a width of 1 dot was printed in parallel with the scanning direction of the head to visually observe it 25 cm apart from the line, thereby evaluating the print quality.

The print quality was ranked as P where the edge portions of the straight line were dim or blurred, and/or feathering occurred markedly or G where the straight line was visually clear.

10 (2) Bronzing tendency (1):

Solid printing was conducted throughout the surface of recording paper by mean of the above-described recording apparatus. The bronzing tendency was ranked as G where the solid printed area visible black or P where bronzing occurred, and brown mottles were hence recognized.

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(3) Bronzing tendency (2)

The chromaticity (L^* , a^* , b^*) of the above printed area was determined by means of a color analyzer CA-35 (manufactured by Murakami Shikisai Kagaku K.K.) to evaluate the bronzing tendency by the value of a^* .

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The value of a^* nearer 0 means that the color of the printed area comes nearer the achromatic color (black). On the other hand, the greater value of a^* means that the color becomes more reddish and visually looks brown.

Table 1

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Examples and Comparative Examples, and evaluation results					
Recording paper	Ink	Evaluation items			Remarks
		(1) Print quality	(2) Bronzing tendency (1)	(3) Bronzing tendency (2)	
A	a	G	G	1.42	Example 1
B	a	G	G	1.57	Example 2
C	a	G	G	1.81	Example 3
35 D	a	G	G	1.60	Example 4
E	a	G	P	3.54	Comp. Ex.1
F	a	P	G	1.33	Comp. Ex.2
A	b	G	G	1.32	Example 5
A	c	G	G	1.08	Example 6
40 A	d	G	G	1.21	Example 7

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While the present invention has been described with respect to what is presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be according to the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

Disclosed herein is recording paper suitable for use in ink-jet recording systems making use of an ink containing a nitrogen compound, comprising neutral or alkaline paper as a base, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink thereon, in the interior thereof.

Claims

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1. Recording paper suitable for use in ink-jet recording systems making use of an ink containing a nitrogen compound, comprising neutral or alkaline paper as a base, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface

thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink thereon, in the interior thereof.

2. The recording paper according to Claim 1, wherein the nitrogen compound is a solubilizer for a dye.

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3. The recording paper according to Claim 1, wherein the adsorbing substance is synthetic aluminum silicate or kaolin minerals.

4. An ink-jet recording process comprising applying an ink containing a dye, a low-boiling solvent and a nonvolatile solvent to neutral or alkaline paper to conduct recording, wherein ink droplets are applied to a recording surface of the neutral or alkaline paper so as to evaporate the low-boiling solvent in the ink on the recording surface, and then to cause the nonvolatile solvent to penetrate into the paper while preventing the orientation of the dye.

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5. An ink-jet recording process comprising conducting recording on neutral or alkaline paper with an ink containing a nitrogen compound as a solubilizer for a dye, wherein the recording paper contains a penetration-retarding agent for retarding the penetration of the ink in a recording surface thereof, and is filled with a substance, which adsorbs ammonia or ammonium ions caused by the nitrogen compound in the ink therein, in the interior thereof.

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6. The ink-jet recording process according to Claim 5, wherein the adsorbing substance is synthetic aluminum silicate or kaolin minerals.

7. The ink-jet recording process according to Claim 5, wherein the nitrogen compound is urea.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 0953

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.5)
A	DATABASE WPI,n 87-216231,Derwent Publications Ltd,GB; & JP-A-62140877(CANON KK) 24-06-1987 *The entire abstract* -----	1-7	B41M5/00
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 May 1994	Examiner Fouquier, J-P
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			