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(54) Ink jet recording element and printing method

Tintanstrahlaufzeichnungselement und Aufzeichnungsverfahren

Elément pour l'impression au jet d'encre et procédé d'impression

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(73) Proprietor: **Eastman Kodak Company**
Rochester, NY 14650-2201 (US)

(72) Inventors:
- **Bermel, Alexandra DeLauro,**
  Eastman Kodak Company
  Rochester,
  New York 14650-2201 (US)
- **Shaw-Klein, Lori Jeanne,**
  c/o Eastman Kodak Company
  Rochester,
  New York 14650-2201 (US)

(74) Representative: **Weber, Etienne Nicolas**
Kodak
Etablissement de Chalon
Campus Industriel - Département Brevets
Route de Demigny - Z.I. Nord - B.P. 21
71102 Chalon-sur-Saône Cedex (FR)

(56) References cited:
EP-A- 0 487 350
EP-A- 0 634 289
EP-A- 0 806 299
EP-A- 0 875 394
EP-A- 0 909 851
EP-A- 1 101 624
EP-A- 1 120 281
DE-A- 19 534 327
US-A- 4 780 356

- **DATABASE WPI Section Ch, Week 199502 Derwent Publications Ltd., London, GB; Class A82, AN 1995-011485 XP002249240 & JP 06 297832 A (ASAHI GLASS CO LTD), 25 October 1994 (1994-10-25)**
- **PATENT ABSTRACTS OF JAPAN vol. 2000, no. 04, 31 August 2000 (2000-08-31) & JP 2000 027093 A (KONICA CORP), 25 January 2000 (2000-01-25)**
- **DATABASE WPI Section Ch, Week 199245 Derwent Publications Ltd., London, GB; Class A14, AN 1992-370547 XP002249241 & JP 04 272888 A (ASAHI GLASS CO LTD), 29 September 1992 (1992-09-29)**
- **PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 058943 A (KONICA CORP), 2 March 1999 (1999-03-02)**
- **DATABASE WPI Section Ch, Week 200059 Derwent Publications Ltd., London, GB; Class A97, AN 2000-614719 XP002249242 & JP 2000 218927 A (KONICA CORP), 8 August 2000 (2000-08-08)**

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Description

[0001] The present invention relates to a porous ink jet recording element and printing method using the element.

[0002] In a typical ink jet recording or printing system, ink droplets are ejected from a nozzle at high speed towards a recording element or medium to produce an image on the medium. The ink droplets, or recording liquid, generally comprise a recording agent, such as a dye or pigment, and a large amount of solvent. The solvent, or carrier liquid, typically is made up of water and an organic material such as a monohydric alcohol, a polyhydric alcohol or mixtures thereof.

[0003] An ink jet recording element typically comprises a support having on at least one surface thereof an ink-receiving or image-receiving layer, and includes those intended for reflection viewing, which have an opaque support, and those intended for viewing by transmitted light, which have a transparent support.

[0004] An important characteristic of ink jet recording elements is their need to dry quickly after printing. To this end, porous recording elements have been developed which provide nearly instantaneous drying as long as they have sufficient thickness and pore volume to effectively contain the liquid ink. For example, a porous recording element can be manufactured by cast coating, in which a particulate-containing coating is applied to a support and is dried in contact with a polished smooth surface.

[0005] When a porous recording element is manufactured, it is difficult to co-optimize the image-receiving layer surface appearance and ink drying times. Good image-receiving layer surface appearance is obtained when it is virtually crack-free. A crack-free surface appearance can be obtained merely by adding more binder to the image-receiving layer. However, adding more binder increases dry time since the binder fills the pores in the image-receiving layer. Therefore, it is difficult to obtain an image-receiving layer which has a crack-free surface yet is fast-drying.

[0006] U.S. Patent 6,037,050 and EP 888,904 relate to an ink jet recording element wherein an ink absorption layer comprises inorganic particles such as silica and a poly(vinyl alcohol) binder that is crosslinked with a hardener. However, there is no disclosure in these references that the poly(vinyl alcohol) binder should have a certain viscosity or that the inorganic particles comprise a fumed metallic oxide.

[0007] It is an object of this invention to provide a porous ink jet recording element that exhibits good overall appearance without cracking and has an excellent dry time. It is another object of the invention to provide a printing method using the above-described element.

[0008] These and other obj ects are achieved in accordance with the invention which comprises an ink jet recording element comprising a support having thereon a porous image-receiving layer comprising particles and a poly(vinyl alcohol) binder, the particles comprising a fumed metallic oxide, and the binder having an average viscosity greater than 25 cp at 4% solids in an aqueous solution at 20°C wherein the weight ratio of said binder to said particles is from 1:20 to 1:5 and wherein said image-receiving layer also contains a crosslinker crosslinking said binder.

[0009] By use of the invention, a porous ink jet recording element is obtained that exhibits good overall appearance without cracking and has an excellent dry time.

[0010] Another embodiment of the invention relates to an ink jet printing method, comprising the steps of:

A) providing an ink jet printer that is responsive to digital data signals;
B) loading said printer with an ink jet recording element as described above;
C) loading said printer with an ink jet ink composition; and
D) printing on said image-receiving layer using said ink jet ink composition in response to said digital data signals.

[0011] Any fumed metallic oxide particles may be used in the invention. Examples of such particles include fumed alumina, silica, titania, cationic silica, antimony(III) oxide, chromium(III) oxide, iron(III) oxide, germanium(IV) oxide, vanadium(V) oxide, or tungsten(VI) oxide. In a preferred embodiment, fumed alumina, fumed silica or cationic fumed silica is employed. Fumed oxides are available in dry form or as dispersions. The fumed metallic oxide particles may be porous or nonporous.

[0012] The fumed metallic oxide particles used in the invention may be in the form of primary particles or in the form of secondary aggregated particles. Preferred aggregates are comprised of smaller primary particles 7 to 40 nm in diameter and are aggregated up to 300 nm in diameter. The pores in a dried coating of such aggregates fall within the range necessary to ensure low optical scatter yet sufficient ink solvent uptake.

[0013] The process for fuming metallic oxides is well known in the art. For example, reference may be made to Technical Bulletin Pigments, no. 56, Highly Dispersed Metallic Oxides Produced by the AEROSIL ® Process, by Degussa AG., 1995.

[0014] Porosity of an image-receiving layer is necessary in order to obtain very fast ink drying. The pores formed between the particles must be sufficiently large and interconnected so that the printing ink passes quickly through the layer and away from the outer surface to give the impression of fast drying. At the same time, the particles must be arranged in such a way so that the pores formed between them are sufficiently small that they do not scatter visible light.

[0015] As noted above, the poly(vinyl alcohols) useful in the invention have an average viscosity greater than 25 cp when employed in a 4% aqueous solids solution at 20°C preferably an average viscosity from 25 to 100 cp and more preferably from 27 to 60 cp at 4% solids aqueous solution at 20°C. Specific examples of such poly(vinyl alcohols) which may be used in the invention include the following:

Table 1

	Poly(vinyl alcohol)	Average Viscosity @ 4% (cp)*
PVA-A	Gohsenol® GH-17	30
PVA-B	Gohsenol® GH-23	52
PVA-C	Gohsenol® N300	27.5
*Trade publication, Nippon Gohsei Co., Ltd.		

[0016] The amount of poly(vinyl alcohol) binder used should be sufficient to impart cohesive strength to the image-receiving layer, but as small as possible so that the interconnected pore structure formed by the aggregates is not filled in by the binder. According to the invention, the weight ratio of the binder to the particles is from 1:20 to 1:5.

[0017] The image-receiving layer may also contain a mordant. Examples of mordants which may be used include water-soluble cationic polymers, metal salts, water-insoluble cationic polymeric particles in the form of a latex, water dispersible polymer, beads, or core/shell particles wherein the core is organic or inorganic and the shell in either case is a cationic polymer. Such particles can be products of addition or condensation polymerization, or a combination of both. They can be linear, branched, hyper-branched, grafted, random, blocked, or can have other polymer microstructures well known to those in the art. They also can be partially crosslinked. Examples of core/shell particles useful in the invention are disclosed and claimed in U.S. Patent Application Serial No. 09/772,097, of Lawrence et al., Ink Jet Printing Method, filed of even date herewith, Docket 81894HEC. Examples of water dispersible particles useful in the invention are disclosed and claimed in U.S. Patent Application Serial No. 09/770,128, of Lawrence et al., Ink Jet Printing Method, filed of even date herewith, Docket 81815HEC; and U.S. Patent Application Serial No. 09/770,127, of Lawrence et al., Ink Jet Printing Method, filed of even date herewith, Docket 81817HEC.

[0018] Examples of crosslinkers which may be used include carbodiimides, polyfunctional aziridines, aldehydes, isocyanates, epoxides, polyvalent metal cations, acetals, ketals, etc. In a preferred embodiment of the invention, the crosslinker is an aldehyde, an acetal or a ketal. In a more preferred embodiment, the crosslinker is 2,3-dihydroxy-1,4-dioxane.

[0019] Since the image-receiving layer is a porous layer comprising particles, the void volume must be sufficient to absorb all of the printing ink. For example, if a porous layer has 60 volume % open pores, in order to instantly absorb 32 cc/m^2 of ink, it must have a physical thickness of at least 54 μm.

[0020] The support for the ink jet recording element used in the invention can be any of those usually used for ink jet receivers, such as resin-coated paper, paper, polyesters, or microporous materials such as polyethylene polymer-containing material sold by PPG Industries, Inc., Pittsburgh, Pennsylvania under the trade name of Teslin ®, Tyvek ® synthetic paper (DuPont Corp.), and OPPalyte® films (Mobil Chemical Co.) and other composite films listed in U.S. Patent 5,244,861. Opaque supports include plain paper, coated paper, synthetic paper, photographic paper support, melt-extrusion-coated paper, and laminated paper, such as biaxially oriented support laminates. Biaxially oriented support laminates are described in U.S. Patents 5,853,965; 5,866,282; 5,874,205; 5,888,643; 5,888,681; 5,888,683; and 5,888,714. These biaxially oriented supports include a paper base and a biaxially oriented polyolefin sheet, typically polypropylene, laminated to one or both sides of the paper base. Transparent supports include glass, cellulose derivatives, e.g., a cellulose ester, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate; polyesters, such as poly(ethylene terephthalate), poly(ethylene naphthalate), poly(1,4-cyclohexanedimethylene terephthalate), poly(butylene terephthalate), and copolymers thereof; polyimides; polyamides; polycarbonates; polystyrene; polyolefins, such as polyethylene or polypropylene; polysulfones; polyacrylates; polyetherimides; and mixtures thereof. The papers listed above include a broad range of papers, from high end papers, such as photographic paper to low end papers, such as newsprint In a preferred embodiment, polyethylene-coated paper is employed.

[0021] The support used in the invention may have a thickness of from 50 to 500 μm, preferably from 75 to 300 μm. Antioxidants, antistatic agents, plasticizers and other known additives may be incorporated into the support, if desired.

[0022] In order to improve the adhesion of the ink-receiving layer to the support, the surface of the support may be subjected to a corona-discharge treatment prior to applying the image-receiving layer.

[0023] Coating compositions employed in the invention may be applied by any number of well known techniques, including dip-coating, wound-wire rod coating, doctor blade coating, gravure and reverse-roll coating, slide coating, bead coating, extrusion coating, curtain coating and the like. Known coating and drying methods are described in further detail

in Research Disclosure no. 308119, published Dec. 1989, pages 1007 to 1008. Slide coating is preferred, in which the base layers and overcoat may be simultaneously applied. After coating, the layers are generally dried by simple evaporation, which may be accelerated by known techniques such as convection heating.

[0024] To improve colorant fade, UV absorbers, radical quenchers or antioxidants may also be added to the image-receiving layer as is well known in the art. Other additives include pH modifiers, adhesion promoters, rheology modifiers, surfactants, biocides, lubricants, dyes, optical brighteners, matte agents, antistatic agents, etc. In order to obtain adequate coatability, additives known to those familiar with such art such as surfactants, defoamers, alcohol and the like may be used. A common level for coating aids is 0.01 to 0.30% active coating aid based on the total solution weight. These coating aids can be nonionic, anionic, cationic or amphoteric. Specific examples are described in MCCUTCHEON's Volume 1: Emulsifiers and Detergents, 1995, North American Edition.

[0025] The coating composition can be coated either from water or organic solvents, however water is preferred. The total solids content should be selected to yield a useful coating thickness in the most economical way, and for particulate coating formulations, solids contents from 10-40% are typical.

[0026] Ink jet inks used to image the recording elements of the present invention are well-known in the art. The ink compositions used in ink jet printing typically are liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, and the like. The solvent or carrier liquid can be solely water or can be water mixed with other water-miscible solvents such as polyhydric alcohols. Inks in which organic materials such as polyhydric alcohols are the predominant carrier or solvent liquid may also be used. Particularly useful are mixed solvents of water and polyhydric alcohols. The dyes used in such compositions are typically water-soluble direct or acid type dyes. Such liquid compositions have been described extensively in the prior art including, for example, U.S. Patents 4,381,946; 4,23 9,543 and 4,781,758.

[0027] The following example is provided to illustrate the invention.

EXAMPLE

[0028] The following are comparative poly(vinyl alcohols) used which have an average viscosity of less than 25 cp at a 4% aqueous solution at 20° C:

Table 2

	Poly(vinyl alcohol)	Average Viscosity @ 4% cp
C-1	Gohsenol® GL-05	5.3[1]
C-2	Gohsenol® GM-14	22.5[1]
C-3	Elvanol® 52-22	23.5[2]
[1]Trade publication, Nippon Gohsei Co., Ltd. [2]Trade publication, DuPont Corp.		

Element 1 of the Invention

[0029] A coating solution was prepared by combining fumed alumina (Cab-O-Sperse® PG003, Cabot Corp.), PVA-A and crosslinker 2,3-dihydroxy-1,4-dioxane (Clariant Corp.) in a ratio of 86:12:2 to give an aqueous coating formulation of 30% solids by weight. The layer was bead-coated at 40°C on polyethylene-coated paper base which had been previously subjected to corona discharge treatment. The coating was then dried at 60°C by forced air to yield a recording element with a thickness of 40 μm.

Element 2 of the Invention

[0030] This element was prepared the same as Element 1 except that PVA-B was used instead of PVA-A.

Element 3 of the Invention

[0031] This element was prepared the same as Element 1 except that PVA-C was used instead of PVA-A.

Element 4 of the Invention

[0032] This element was prepared the same as Element 2 except that fumed silica, CEP10AK97001, aqueous dis-

persion, (Cabot Corp.) was used instead of fumed alumina.

Element 5 of the Invention

[0033] This element was prepared the same as Element 2 except that cationic fumed silica, CEP10AK97006, aqueous dispersion, (Cabot Corp.) was used instead of fumed alumina.

Comparative Element C-1

[0034] This element was prepared the same as Element 1 except that C-1 was used instead of PVA-A.

Comparative Element C-2

[0035] This element was prepared the same as Element 1 except that C-2 was used instead of PVA-A.

Comparative Element C-3

[0036] This element was prepared the same as Element 4 except that C-3 was used instead of PVA-A.

Comparative Element C-4

[0037] This element was prepared the same as Element 2 except that colloidal alumina, Dispal® 11N7-80, alumina powder, (Condea Vista Co.) was used instead of fumed alumina.

Coating Quality

[0038] The above dried coatings were visually evaluated for cracking defects and were rated as follows:

0 = no cracking
1 = slight cracking at the coating edges
2 = cracking at the coating edges
3 = cracking throughout the coating
4 = sample severely cracked throughout the coating
5 = sample severely cracked and flaked off the support

Table 3

Recording Element	Cracking Rating
1	0
2	0
3	0
4	0
5	0
C-1	5
C-2	2
C-3	2
C-4	0

[0039] The above results show that the image-receiving layer of the elements of the invention did not crack. Although the image-receiving layer of comparative element C-4 also did not crack, it had other problems as will be shown below in Table 4.

Dry Time

[0040] Test images of cyan, magenta, yellow, red, green, blue and black bars, each 1.1 cm by 13.5 cm, were printed on the above elements using an Epson Stylus® Photo 870 using inks with catalogue number T008241. Immediately after ejection from the printer, a piece of bond paper was placed over the printed image and rolled with a smooth, heavy weight. Then the bond paper was separated from the printed image. Ink transferred to the bond paper if the recording element was not dry. The length of the bar imaged on the bond paper was measured and is proportional to the dry time. Dry times corresponding to a length of about 40 cm or less are acceptable.

Table 4

Recording Element	Proportional Dry Time (cm)
1	34
2	17
3	27
4	0
C-1	*
C-2	29.5
C-3	0
C-4	65
* Was too cracked to print on to get a measurement	

[0041] The above results show that the elements of the invention had better dry times than all the comparative elements except for C-3. However, C-3 had other problems as shown above in Table 3. Only the recording elements of the invention were good for both cracking and dry time.

Claims

1. An inkjet recording element comprising a support, having thereon a porous image-receiving layer comprising particles and a poly(vinyl alcohol) binder, said particles comprising a fumed metallic oxide, and said binder having an average viscosity greater than 25 cp at 4% solids in an aqueous solution at 20°C, wherein the weight ratio of said binder to said particles is from 1:20 to 1:5 and wherein said image-receiving layer also contains a crosslinker crosslinking said binder.

2. The recording element of Claim 1 wherein said average viscosity is from 25 to 100 cp.

3. The recording element of Claim 1 wherein said average viscosity is from 27 to 60 cp.

4. The recording element of Claim 1 wherein said crosslinker is an aldehyde, an acetal or a ketal.

5. The recording element of Claim 1 wherein said crosslinker is 2,3-dihydroxy-1,4-dioxane.

6. The recording element of Claim 1 wherein said support is polyethylene-coated paper.

7. The recording element of Claim 1 wherein said image-receiving layer also contains a mordant.

8. An ink jet printing method, comprising the steps of:

   A) providing an ink jet printer that is responsive to digital data signals;
   B) loading said printer with an ink jet recording element as described in Claim 1;
   C) loading said printer with an inkjet ink composition; and
   D) printing on said image-receiving layer using said ink jet ink composition in response to said digital data signals.

Patentansprüche

1. Tintenstrahlaufzeichnungselement mit einem Träger, auf dem sich eine poröse Bildempfangsschicht befindet, die Feststoffteilchen und ein Bindemittel auf der Basis von Polyvinylalkohol umfasst, wobei die Feststoffteilchen ein pyrogenes Metalloxid aufweisen und das Bindemittel bei einem Gehalt von 4 % Feststoff in einer wässrigen Lösung bei 20°C eine mittlere Viskosität von mehr als 25 Cp aufweist, worin das Gewichtsverhältnis des Bindemittels zu den Teilchen zwischen 1:20 und 1:5 beträgt und worin die Bildempfangsschicht zudem ein Vernetzungsmittel enthält, das das Bindemittel vernetzt.

2. Aufzeichnungselement nach Anspruch 1, worin die mittlere Viskosität zwischen 25 und 100 Cp liegt.

3. Aufzeichnungselement nach Anspruch 1, worin die mittlere Viskosität zwischen 27 und 60 Cp liegt.

4. Aufzeichnungselement nach Anspruch 1, worin das Vernetzungsmittel ein Aldehyd, ein Acetal oder ein Ketal ist.

5. Aufzeichnungselement nach Anspruch 1, worin das Vernetzungsmittel 2,3-Dihydroxy-1,4-dioxan ist.

6. Aufzeichnungselement nach Anspruch 1, worin der Träger mit Polyethylen beschichtetes Papier ist.

7. Aufzeichnungselement nach Anspruch 1, worin die Bildempfangsschicht auch ein Beizmittel enthält.

8. Tintenstrahl-Druckverfahren, mit folgenden Schritten:

   A) Bereitstellung eines Tintenstrahldruckers, der auf digitale Datensignale anspricht;
   B) Beladung des Druckers mit einem Tintenstrahl-Aufzeichnungselement nach Anspruch 1;
   C) Beladung des Druckers mit einer Tintenstrahltintenkomposition; und
   D) Bedrucken der Bildempfangsschicht mit der Tintenstrahltintenkomposition in Abhängigkeit von den digitalen Datensignalen.

Revendications

1. Elément pour l'enregistrement par jet d'encre comprenant un support revêtu d'une couche réceptrice d'image poreuse comprenant des particules et un liant d'alcool polyvinylique, lesdites particules comprenant un oxyde métallique calciné et ledit liant ayant une viscosité moyenne supérieure à 25 cp à raison d'une teneur en solides de 4% dans une solution aqueuse à 20°C dans lequel le rapport en poids dudit liant auxdites particules est compris entre 1 :20 et 1 :5 et dans lequel la couche réceptrice d'image contient aussi un agent réticulant qui réticule ledit liant.

2. Elément pour l'enregistrement selon la revendication 1, dans lequel ladite viscosité moyenne est comprise entre 25 et 100 cp.

3. Elément pour l'enregistrement selon la revendication 1, dans lequel ladite viscosité moyenne est comprise entre 27 et 60 cp.

4. Elément pour l'enregistrement selon la revendication 1, dans lequel ledit agent réticulant est un aldéhyde, un acétal ou un cétal.

5. Elément pour l'enregistrement selon la revendication 1, dans lequel ledit agent réticulant est le 2,3-dihydroxy-1,4-dioxane.

6. Elément pour l'enregistrement selon la revendication 1, dans lequel ledit support est du papier revêtu de polyéthylène.

7. Elément pour l'enregistrement selon la revendication 1, dans lequel ladite couche réceptrice d'image contient également un mordant.

8. Procédé d'impression par jet d'encre, comprenant les étapes suivantes :

   A) disposer d'une imprimante à jet d'encre sensible à des signaux de données numériques ;

B) charger dans ladite imprimante un élément pour l'enregistrement par jet d'encre tel que décrit dans la revendication 1 ;
C) charger dans ladite imprimante une composition d'encre pour jet d'encre, et
D) imprimer sur ladite couche réceptrice d'image en utilisant ladite encre pour jet d'encre en réponse auxdits signaux de données numériques.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 6037050 A **[0006]**
- EP 888904 A **[0006]**
- US 772097 A **[0017]**
- US 770128 A **[0017]**
- US 770127 A **[0017]**
- US 5244861 A **[0020]**
- US 5853965 A **[0020]**
- US 5866282 A **[0020]**
- US 5874205 A **[0020]**
- US 5888643 A **[0020]**
- US 5888681 A **[0020]**
- US 5888683 A **[0020]**
- US 5888714 A **[0020]**
- US 4381946 A **[0026]**
- US 4239543 A **[0026]**
- US 4781758 A **[0026]**

Non-patent literature cited in the description

- *Research Disclosure,* (308119), 1007 **[0023]**