

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 288 008 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
**14.12.2005 Bulletin 2005/50**

(51) Int Cl.7: **B41M 5/00**

(21) Application number: **02078397.3**

(22) Date of filing: **16.08.2002**

### (54) Ink jet recording element and printing method

Tintenstrahlaufzeichnungselement und Druckverfahren

Élément pour impression par jet d'encre et procédé d'impression

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **31.08.2001 US 944971**  
**31.08.2001 US 945085**

(43) Date of publication of application:  
**05.03.2003 Bulletin 2003/10**

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**EP 1 288 008 B1**

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**Description**

**[0001]** The present invention relates to a porous ink jet recording element and a 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 printed with dye-based inks, the dye molecules penetrate the coating layers. However, there is a problem with such porous recording elements in that the optical densities of images printed thereon are lower than one would like. The lower optical densities are believed to be due to optical scatter which occurs when the dye molecules penetrate too far into the porous layer.

**[0006]** EP 1,002,660 relates to a porous ink jet recording element comprising fine particles, hydrophilic binder and a water-soluble, cationic polymer. However, there is a problem with this element in that the density of an image printed on such an element using a water-soluble cationic polymer is lower than one would like.

**[0007]** U.S. Patent 6,089,704 relates to a nonporous ink jet recording element comprising cationic polymeric vinyl latex and a hydrophilic polymer. However, there is a problem with this nonporous recording element in that it images printed thereon dry too slowly.

**[0008]** U.S. Patent 6,096,469 relates to an ink jet recording element comprising mesoporous particles dispersed in an organic binder. In column 8, it is disclosed that the organic binder can be a cationic latex polymer "having less than 10 mole percent of a copolymerizable monomer having a tertamino or quaternary ammonium functionality." However, there is a problem with this element in that the density of an image printed on such an element with a binder having less than 10 mole percent of a cationic mordant functionality is lower than one would like.

**[0009]** WO-A-9939914 discloses an image-receiving layer in which the amount of binder is at least 30 weight percent. Inorganic particles are used as mordants rather than to create a porous image-receiving layer. The recording element of WO-A-9939914 is an example of a non-porous media that absorbs ink by diffusion, rather than capillary action as in porous media. Similarly, US-A-5418078 and EP-A-0956971 disclose non-porous image-receiving layers comprising a cationic polymer. EP-A-1034940 discloses cationic polymers that are either water-soluble or soluble in a solvent mixture of water and water miscible organic solvents when coated, hence, not in the form of particles.

**[0010]** It is an object of this invention to provide a porous ink jet recording element that, when printed with dye-based inks, provides superior optical densities, good image quality and has an excellent dry time.

**[0011]** Another object of the invention is to provide a printing method using the above-described element.

**[0012]** These and other objects 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:

- (a) inorganic particles having a mean particle size of from 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$ ; and
- (b) water insoluble, cationic, polymeric particles comprising at least 20 mole percent of a cationic mordant moiety; and
- (c) polymeric binder in an amount up to 20 weight percent in an amount insufficient to alter the porosity of the porous image-receiving layer.

**[0013]** By use of the invention, a porous ink jet recording element is obtained that, when printed with dye-based inks, provides superior optical densities, good image quality and has an excellent dry time.

**[0014]** The invention also relates to an inkjet printing method comprising the steps of

- I) providing an ink jet printer that is responsive to digital data signals;
- II) loading the printer with the porous ink jet recording element described above;
- III) loading the printer with an ink jet ink composition; and
- IV) printing on the above described image-receiving layer using the ink jet ink composition in response to the digital data signals.

**[0015]** In a preferred embodiment, the (a) inorganic particles useful in the invention include alumina, boehmite, hydrated aluminum oxide, clay, calcium carbonate, titanium dioxide, calcined clay, aluminosilicates, silica, and barium sulfate. The (a) inorganic particles may be porous or nonporous. In a preferred embodiment of the invention, the particles are inorganic oxides. In another preferred embodiment, the (a) inorganic particles have a mean particle size of

from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ .  
**[0016]** While many types of inorganic particles are manufactured by various methods and commercially available for an image-receiving layer, porosity of the ink-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.

**[0017]** The (b) water insoluble, cationic, polymeric particles comprising at least 20 mole percent of a cationic mordant moiety useful in the invention can be 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 January 26, 2001. 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 January 26, 2001; and U.S. Patent Application Serial No. 09/770,127, of Lawrence et al., Ink Jet Printing Method, filed January 26, 2001. In a preferred embodiment, the water insoluble, cationic, polymeric particles comprise at least 50 mole percent of a cationic mordant moiety.

**[0018]** The (b) water insoluble, cationic, polymeric particles useful in the invention can be derived from nonionic, anionic, or cationic monomers. In a preferred embodiment, combinations of nonionic and cationic monomers are employed. In general, the amount of cationic monomer employed in the combination is at least 20 mole percent.

**[0019]** The nonionic, anionic, or cationic monomers employed can include neutral, anionic or cationic derivatives of addition polymerizable monomers such as styrenes, alpha-alkylstyrenes, acrylate esters derived from alcohols or phenols, methacrylate esters, vinylimidazoles, vinylpyridines, vinylpyrrolidinones, acrylamides, methacrylamides, vinyl esters derived from straight chain and branched acids (e.g., vinyl acetate), vinyl ethers (e.g., vinyl methyl ether), vinyl nitriles, vinyl ketones, halogen-containing monomers such as vinyl chloride, and olefins, such as butadiene.

**[0020]** The nonionic, anionic, or cationic monomers employed can also include neutral, anionic or cationic derivatives of condensation polymerizable monomers such as those used to prepare polyesters, polyethers, polycarbonates, polyureas and polyurethanes.

**[0021]** The (b) water insoluble, cationic, polymeric particles employed in this invention can be prepared using conventional polymerization techniques including, but not limited to bulk, solution, emulsion, or suspension polymerization.

**[0022]** The amount of (b) water insoluble, cationic, polymeric particles used should be high enough so that the images printed on the recording element will have a sufficiently high density, but low enough so that the interconnected pore structure formed by the aggregates is not filled. In a preferred embodiment of the invention, the weight ratio of (b) water insoluble, cationic, polymeric particles to (a) particles is from 1:2 to 1:10, preferably 1:5.

**[0023]** Examples of (b) water insoluble, cationic, polymeric particles which may be used in the invention include those described in U.S. Patent 3,958,995. Specific examples of these polymers include:

Polymer A. Copolymer of (vinylbenzyl)trimethylammonium chloride and divinylbenzene (87:13 molar ratio)

Polymer B. Terpolymer of styrene, (vinylbenzyl)dimethylbenzylamine and divinylbenzene (49.5:49.5:1.0 molar ratio)

Polymer C. Terpolymer of butyl acrylate, 2-aminoethylmethacrylate hydrochloride and hydroxyethylmethacrylate (50:20:30 molar ratio)

Polymer D. Copolymer of styrene, dimethylacrylamide, vinylbenzylimidazole and 1-vinylbenzyl-3-hydroxyethylimidazolium chloride (40:30:10:20 molar ratio)

Polymer E. Copolymer of styrene, 4-vinylpyridine and N-(2-hydroxyethyl)-4-vinylpyridinium chloride (30:38:32 molar ratio)

Polymer F. Copolymer of styrene, (vinylbenzyl)dimethyloctylammonium chloride, isobutoxymethyl acrylamide and divinylbenzene (40:20:34:6 molar ratio)

**[0024]** The image-receiving layer also contains a polymeric binder in an amount up to 20 weight percent in an amount insufficient to alter the porosity of the porous receiving layer. In another preferred embodiment, the polymeric binder is a hydrophilic polymer such as poly(vinyl alcohol), poly(vinyl pyrrolidone), gelatin, cellulose ethers, poly(oxazolines), poly(vinylacetamides), partially hydrolyzed poly(vinyl acetate/vinyl alcohol), poly(acrylic acid), poly(acrylamide), poly(alkylene oxide), sulfonated or phosphated polyesters and polystyrenes, casein, zein, albumin, chitin, chitosan, dextran, pectin, collagen derivatives, collodian, agar-agar, arrowroot, guar, carrageenan, tragacanth, xanthan, rhaman and

the like. In still another preferred embodiment of the invention, the hydrophilic polymer is poly(vinyl alcohol), hydroxypropyl cellulose, hydroxypropyl methyl cellulose, gelatin, or a poly(alkylene oxide). In yet still another preferred embodiment, the hydrophilic binder is poly(vinyl alcohol). The polymeric binder should be chosen so that it is compatible with the aforementioned particles.

**[0025]** The amount of binder used should be sufficient to impart cohesive strength to the ink jet recording element, but should also be minimized so that the interconnected pore structure formed by the aggregates is not filled in by the binder. In a preferred embodiment of the invention, the weight ratio of the binder to the total amount of particles is from 1:20 to 1:5.

**[0026]** In addition to the image-receiving layer, the recording element may also contain a base layer, next to the support, the function of which is to absorb the solvent from the ink. Materials useful for this layer include (a) particles, (b) particles, polymeric binder and/or crosslinker.

**[0027]** 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<sup>2</sup> of ink, it must have a physical thickness of at least 54  $\mu$ m.

**[0028]** 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.

**[0029]** The support used in the invention may have a thickness of from 50 to 500  $\mu$ m, preferably from 75 to 300  $\mu$ m. Antioxidants, antistatic agents, plasticizers and other known additives may be incorporated into the support, if desired.

**[0030]** 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.

**[0031]** 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, rod coating, air knife 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.

**[0032]** In order to impart mechanical durability to an ink jet recording element, crosslinkers which act upon the binder discussed above may be added in small quantities. Such an additive improves the cohesive strength of the layer. Crosslinkers such as carbodiimides, polyfunctional aziridines, aldehydes, isocyanates, epoxides, polyvalent metal cations, and the like may all be used.

**[0033]** 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 MCCUTCH-  
EON's Volume 1: Emulsifiers and Detergents, 1995, North American Edition.

**[0034]** 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.

**[0035]** 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; 4,239,543 and 4,781,758.

**[0036]** The following example is provided to illustrate the invention.

**[0037]** The following comparative cationic polymers used are water-soluble:

C-1 Poly(vinylbenzyl)trimethylammonium chloride, available as Chemistat® 6300H from Sanyo Chemical Industries.

C-2 Polypropylene oxide-based triamine, available as Jeffamine® T-5000 from Huntsman, Corp.

#### Element 1 of the Invention

**[0038]** A coating solution for a base layer was prepared by mixing 100 dry g of precipitated calcium carbonate Albagloss-s® (Specialty Minerals Inc.) as a 70% solution and 8.5 dry g of silica gel Gasil® 23F (Crosfield Ltd.) with 0.5 dry g of a poly(vinyl alcohol) Gohsenol® GH-17 (Nippon Gohsei Co., Ltd.) as a 10% solution and 5 dry g of styrene-butadiene latex CP692NA® (Dow Chemical) as a 50% solution. The solids of the coating solution was adjusted to 35% by adding water.

**[0039]** The base layer coating solution was bead-coated at 25°C on a base paper, basis weight 185 g/m<sup>2</sup>, and dried at 60°C by forced air. The thickness of the base coating was 25 µm or 27 g/m<sup>2</sup>.

**[0040]** A coating solution for the image-receiving layer was prepared by combining alumina Dispal® 14N4-80 (Condea Vista Co.), poly(vinyl alcohol) Gohsenol® GH-17 (Nippon Gohsei Co.) and Polymer A illustrated above in a ratio of 86:4:10 to give an aqueous coating formulation of 15% solids by weight. Surfactants Zonyl® FS-300 (DuPont Co.) and Silwet® L-7602 (Witco Corp.) were added in small amounts as coating aids.

**[0041]** The image-receiving layer coating solution was coated on top of this base layer. The recording element was then dried at 60 °C by forced air to yield a two-layer recording element. The thickness of the image-receiving layer was 8 µm or 8.6 g/m<sup>2</sup>.

#### Element 2 of the Invention

**[0042]** Element 2 was prepared the same as Element 1 except that Polymer B was used instead of Polymer A.

#### Element 3 of the Invention

**[0043]** Element 3 was prepared the same as Element 1 except that both Polymer A. and Polymer B were used.

#### Comparative Element 1 (no water-insoluble, cationic polymeric particles)

**[0044]** This element was prepared the same as Element 1 except that water-soluble Polymer C-1 was used instead of Polymer A.

#### Comparative Element 2 (no water-insoluble, cationic polymeric particles)

**[0045]** This element was prepared the same as Element 1 except that water-soluble Polymer C-2 was used instead of Polymer A.

#### Comparative Element 3 (no cationic polymeric particles)

**[0046]** This element was prepared the same as Element 1 except that the image-receiving layer contained only alumina and poly (vinyl alcohol) in the ratio 96:4.

#### Density Testing

**[0047]** Test images of cyan, magenta, yellow, red, green and blue patches at 100% ink laydown were printed using a Hewlett-Packard DeskJet 970 printer and ink cartridge with catalogue number HP C6578D.

**[0048]** After drying for 24 hours at ambient temperature and humidity, the Status A D-max densities were measured using an X-Rite® 820 densitometer (for each of the red, green and blue densities, the two component color densities were measured and averaged). The following results were obtained:

Table 1

Recording Element	Status A D-max Density					
	Cyan	Magenta	Yellow	Red	Green	Blue
1	0.9	2	1.6	1.5	1.2	1.6
2	0.9	2	1.6	1.5	1.2	1.6
3	0.9	1.9	1.6	1.5	1.2	1.6
C-1	0.6	1.6	1.2	1.2	1.0	1.2
C-2	0.7	1.7	1.3	1.2	1.1	1.3
C-3	0.9	1.2	1.2	1.2	1.1	1.4

**[0049]** The above results show that Status A D-max densities for the recording element of the invention are higher in all colors as compared to the comparative elements.

## Claims

1. An ink jet recording element comprising a support having thereon a porous image-receiving layer comprising:
  - (a) inorganic particles having a mean particle size of from 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$ ;
  - (b) water insoluble, cationic, polymeric particles comprising at least 20 mole percent of a cationic mordant moiety; and
  - (c) polymeric binder in an amount up to 20 weight percent in an amount insufficient to alter the porosity of the porous image-receiving layer.
2. The recording element of Claim 1 wherein the weight ratio of (b) water insoluble, cationic, polymeric particles to (a) inorganic particles is from 1:2 to 1:10.
3. The recording element of Claim 1 wherein said polymeric binder is a hydrophilic polymer.
4. The recording element of Claim 3 wherein said hydrophilic polymer is poly(vinyl alcohol), hydroxypropyl cellulose, hydroxypropyl methyl cellulose, gelatin, or a poly(alkylene oxide).
5. The recording element of Claim 1 wherein said (a) inorganic particles are inorganic oxides.
6. The recording element of Claim 1 wherein said (a) inorganic particles are silica, alumina, boehmite or hydrated aluminum oxide.
7. An ink jet printing method comprising the steps of:
  - I) providing an ink jet printer that is responsive to digital data signals;
  - II) loading said printer with the porous ink jet recording element of Claim 1;
  - III) loading said printer with an ink jet ink composition; and
  - IV) printing on said image-receiving layer using said ink jet ink composition in response to said digital data signals.

## Patentansprüche

1. Tintenstrahlauzeichnungselement aus einem Träger und einer darauf befindlichen porösen Bildempfangsschicht mit:
  - a) anorganischen Partikeln mit einer mittleren Partikelgröße von 0,05  $\mu\text{m}$  bis 5  $\mu\text{m}$ ;
  - b) wasserunlöslichen, kationischen Polymerpartikeln, die mindestens 20 Mol% eines kationischen Beizmittel-

restes umfassen; und

c) Polymerbindemitteln in einer Menge von bis zu 20 Gew.% in einer Menge, die ausreicht, um die Porosität der porösen Bildempfangsschicht zu verändern.

2. Tintenstrahlaufzeichnungselement nach Anspruch 1, worin das Gewichtsverhältnis von b) wasserunlöslichen, kationischen Polymerpartikeln zu a) anorganischen Partikeln zwischen 1:2 und 1:10 beträgt.

3. Tintenstrahlaufzeichnungselement nach Anspruch 1, worin das Polymerbindemittel ein hydrophiles Polymer ist.

4. Tintenstrahlaufzeichnungselement nach Anspruch 3, worin das Polymerbindemittel Poly(vinylalkohol), Hydroxypropylcellulose, Hydroxypropylmethylcellulose, Gelatine oder Poly(alkylenoxid) ist.

5. Tintenstrahlaufzeichnungselement nach Anspruch 1, worin die a) anorganischen Partikel anorganische Oxide sind.

6. Tintenstrahlaufzeichnungselement nach Anspruch 1, worin die a) anorganischen Partikel Siliciumdioxid, Aluminiumoxid, Boehmit oder hydriertes Aluminiumoxid sind.

7. Tintenstrahldruckverfahren mit folgenden Schritten:

I) Bereitstellen eines Tintenstrahldruckers, der auf digitale Datensignale anspricht;

II) Laden des Druckers mit dem porösen Tintenstrahlaufzeichnungselement nach Anspruch 1;

III) Laden des Druckers mit einer Tintenstrahl-tintenzusammensetzung; und

IV) Bedrucken der Bildempfangsschicht mithilfe der Tintenstrahl-tintenzusammensetzung in Abhängigkeit von den digitalen Datensignalen.

## Revendications

1. Élément pour l'impression par jet d'encre comprenant un support revêtu d'une couche réceptrice d'image poreuse comprenant :

(a) des particules inorganiques ayant une taille moyenne de particule comprise entre 0,05  $\mu\text{m}$  et 5  $\mu\text{m}$  ;

(b) des particules polymères cationiques insolubles dans l'eau comprenant au moins 20% en moles d'un radical de type mordant cationique ; et

(c) une quantité de liant polymère pouvant atteindre 20% en poids en quantité insuffisante pour modifier la porosité de la couche réceptrice d'image poreuse.

2. Élément pour l'impression selon la revendication 1, dans lequel le rapport en poids des particules polymères cationiques insolubles dans l'eau (b) aux particules inorganiques (a) est compris entre 1:2 et 1:10.

3. Élément pour l'impression selon la revendication 1, dans lequel ledit liant polymère est un polymère hydrophile.

4. Élément pour l'impression selon la revendication 3, dans lequel ledit polymère hydrophile est l'alcool polyvinylique, l'hydroxypropyl cellulose, l'hydroxypropyl méthyl cellulose, la gélatine ou un polyoxyalkylène.

5. Élément pour l'impression selon la revendication 1, dans lequel lesdites particules inorganiques (a) sont des oxydes inorganiques.

6. Élément pour l'impression selon la revendication 1, dans lequel lesdites particules inorganiques (a) sont la silice, l'alumine, la boehmite ou l'oxyde d'aluminium hydraté.

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

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

II) charger dans ladite imprimante l'élément pour l'impression par jet d'encre poreux de la revendication 1 ;

III) charger dans ladite imprimante une composition d'encre pour jet d'encre, et

IV) imprimer sur ladite couche réceptrice d'image en utilisant ladite encre pour jet d'encre en réponse auxdits signaux de données numériques.