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

(57) An ink jet recording element comprising a support having thereon porous image-receiving layer comprising particles, a poly(vinyl alcohol) binder and a crosslinking agent, the particles having a primary particle size of from 7 to 40 nm in diameter which may be aggregated up to 300 nm, and the crosslinking agent being present in an amount of at least 20 weight % of the poly(vinyl alcohol) binder and printing method using same.

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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] Another problem encountered with a recording element is ink coalescence which occurs when adjacent ink dots coalesce which leads to nonuniform density.

[0007] 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 crosslinker should be present in an amount greater than 10%, based on the binder.

[0008] 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 and reduced ink coalescence. It is another object of the invention to provide a printing method using the above-described element.

[0009] 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 particles, a poly(vinyl alcohol) binder and a crosslinking agent, the particles having a primary particle size of from 7 to 40 nm in diameter which may be aggregated up to 300 nm, and the crosslinking agent being present in an amount of at least 20 weight % of the poly (vinyl alcohol) binder.

[0010] 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 and reduced ink coalescence.

[0011] 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 the 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.

[0012] Examples of particles useful in the invention include alumina, boehmite, clay, calcium carbonate, titanium dioxide, calcined clay, aluminosilicates, silica, barium sulfate, or polymeric beads. The particles may be porous or nonporous. In a preferred embodiment of the invention, the particles are metallic oxides, preferably fumed. While many types of inorganic and organic 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. 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.

[0013] The particles may be in the form of primary particles, or in the form of secondary aggregated particles. The aggregates are comprised of smaller primary particles 7 to 40 nm in diameter, and being 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.

[0014] 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. Preferred examples of fumed metallic oxides which may be used in the invention include silica and alumina fumed oxides. Fumed oxides are available in dry form or as dispersions of the aggregates mentioned above.

[0015] 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 DegussaAG., 1995.

[0016] Any poly(vinyl alcohol) may be used in the invention. In a preferred embodiment, the poly(vinyl alcohol) has an average viscosity greater than 20 cp when employed in a 4% aqueous solids 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[1]
PVA-B	Gohsenol® GH-23	52[1]
PVA-C	Gohsenol® N300	27.5[1]
PVA-D	Elvanol® 52-22	23.5[2]

[1]Trade publication, Nippon Gohsei Co., Ltd.
[2]Trade publication, DuPont Corp.

[0017] 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. In a preferred embodiment of the invention, the weight ratio of the binder to the particles is from 1:20 to 1:5.

[0018] 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. 09/70,127, of Lawrence et al., Ink Jet Printing Method, filed of even date herewith, Docket 81817HEC.

[0019] Examples of crosslinkers which may be used in the invention 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.

[0020] As noted above, the amount of crosslinking agent is present in an amount of at least 20 weight % of the poly (vinyl alcohol) binder. This amount is far beyond a typical amount of crosslinking agent for poly(vinyl alcohol). For example, in Paper Coating Additives, Robert J. Kane, TAPPI PRESS, Atlanta Ga., 1995, page 96, it is disclosed that a typical aldehyde crosslinker, glyoxal, is used at 10% by weight relative to the poly(vinyl alcohol). In a preferred embodiment of the invention, the crosslinking agent is present in an amount of at least 40 weight %, more preferably 50 weight %, of the poly(vinyl alcohol) binder.

[0021] 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.

[0022] 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.

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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.

[0029] The following example is provided to illustrate the invention.

EXAMPLE

Element 1 of the Invention

[0030] A coating solution was prepared by combining fumed alumina (Cab-O-Sperse® PG003, Cabot Corp.), PVA-B and crosslinker 2,3-dihydroxy-1,4-dioxane (Clariant Corp.) in a ratio of 88:10:2 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 20 weight % of the poly(vinyl alcohol) binder.

[0031] 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

[0032] This element was prepared the same as Element 1 except that the ratio of components was 87:10:3 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 30 weight % of the poly(vinyl alcohol) binder.

Element 3 of the Invention

[0033] This element was prepared the same as Element 1 except that the ratio of components was 86:10:4 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 40 weight % of the poly(vinyl alcohol) binder.

Comparative Element C-1

[0034] This element was prepared the same as Element 1 except that PVA-D was used instead of PVA-B, and the ratio of components was 84:15:1 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 6.6 weight % of the poly(vinyl alcohol) binder.

Comparative Element C-2

[0035] This element was prepared the same as Element 1 except that PVA-D was used instead of PVA-B, and the ratio of components was 86.5:12.5:1 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 8 weight % of the poly(vinyl alcohol) binder.

Comparative Element C-3

[0036] This element was prepared the same as Element 1 except that PVA-D was used instead of PVA-B, and the ratio of components was 89:10:1 to give an aqueous coating formulation of 30% solids by weight, so that the crosslinking agent is present in an amount of 10 weight % of the poly(vinyl alcohol) binder.

Coating Quality

[0037] The above dried coatings were visually evaluated for cracking with the following results:

Table 2

Recording Element	Cracking
1	None
2	None
3	None
C-1	None
C-2	None
C-3	Some

[0038] The above results show that neither any of the recording elements of the invention nor two comparative elements exhibited any cracking.

Dry Time

[0039] 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 T008201. 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 3

Recording Element	Proportional Dry Time (cm)
1	6
2	2
3	6
C-1	91

Table 3 (continued)

Recording Element	Proportional Dry Time (cm)
C-2	91
C-3	65

[0040] The above results show that the elements of the invention had much better dry times than all the comparative elements.

Coalescence

[0041] A test image of a green patch was printed on each of the above elements using an Epson Stylus® Photo 870 using inks with catalogue number T008201. Coalescence of the ink on the patches was visually rated as follows:

1 = None
2 = Slight
3 = Moderate
4 = Severe

[0042] The following results were obtained:

Table 4

Recording Element	Coalescence
1	3
2	2
3	1
C-1	4
C-2	4
C-3	4

[0043] The above results show that the recording elements of the invention had much less coalescence than the comparative elements.

Claims

1. An ink jet recording element comprising a support having thereon a porous image-receiving layer comprising particles, a poly(vinyl alcohol) binder and a crosslinking agent, said particles having a primary particle size of from 7 to 40 nm in diameter which may be aggregated up to 300 nm, and said crosslinking agent being present in an amount of at least 20 weight % of said poly(vinyl alcohol) binder.

2. The recording element of Claim 1 wherein said crosslinking agent is present in an amount of at least 40 weight % of said poly(vinyl alcohol) binder.

3. The recording element of Claim 1 wherein said crosslinking agent is present in an amount of at least 50 weight % of said poly(vinyl alcohol) binder.

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. The recording element of Claim 1 wherein the weight ratio of said binder to said particles is from 1:20 to 1:5.

9. The recording element of Claim 1 wherein said particles are metallic oxides.

10. 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 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.