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(54) Ink jet recording element and priting method

(57) An ink jet recording element comprising a support having thereon an image-receiving layer, the ink jet recording element containing a metal(oxy)hydroxide complex, $M^{n+}(O)_a(OH)_b(A^{p-})_c \cdot xH_2O$, wherein M is at least one metal ion; n is 3 or 4; A is an organic or inorganic ion; p is 1, 2 or 3; and x is equal to or greater than 0; with the proviso that when n is 3, then a, b and c each comprise a rational number as follows: $0 \leq a < 1.5$; $0 < b < 3$; and $0 \leq pc < 3$, so that the charge of the M^{3+} metal ion is balanced; and when n is 4, then a, b and c each comprise a rational number as follows: $0 \leq a < 2$; $0 < b < 4$; and $0 \leq pc < 4$, so that the charge of the M^{4+} metal ion is balanced.

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Description

[0001] The present invention relates to an ink jet recording element containing a stabilizer 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 coating in which a particulate-containing coating is applied to a support and is dried.

[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. Another problem with a porous recording element is that atmospheric gases or other pollutant gases readily penetrate the element and lower the optical density of the printed image causing it to fade.

[0006] EP 1 016 543 relates to an ink jet recording element containing aluminum hydroxide in the form of boehmite. However, there is a problem with this element in that it is not stable to light and exposure to atmospheric gases.

[0007] EP 0 965 460A2 relates to an ink jet recording element containing aluminum hydrate having a boehmite structure and a non-coupling zirconium compound. However, there is no specific teaching of a metal oxy(hydroxide) complex as described herein.

[0008] U.S. Patent 5,372,884 relates to ink jet recording elements containing a hydrous zirconium oxide. However, there is a problem with such elements in that they tend to fade when subjected to atmospheric gases, as will be shown hereafter.

[0009] It is an object of this invention to provide an ink jet recording element that, when printed with dye-based inks, provides superior optical densities, good image quality and has an excellent dry time.

[0010] Still another object of the invention is to provide a printing method using the above described element.

[0011] This and other objects are achieved in accordance with the invention which comprises an ink jet recording element comprising a support having thereon an image-receiving layer, the ink jet recording element containing a metal (oxy)hydroxide complex,

$$M^{n+}(O)_a(OH)_b(A^{P-})_c \bullet xH_2O,$$

wherein

M is at least one metal ion;
n is 3 or 4;
A is an organic or inorganic ion;
pis 1, 2 or 3; and
x is equal to or greater than 0;
with the proviso that when n is 3, then a, b and c each comprise a rational number as follows: $0 \leq a < 1.5$; $0 < b < 3$; and $0 \leq pc < 3$, so that the charge of the M^{3+} metal ion is balanced;
and when n is 4, then a, b and c each comprise a rational number as follows: $0 \leq a < 2$; $0 < b < 4$; and $0 \leq pc < 4$, so that the charge of the M^{4+} metal ion is balanced.

[0012] By use of the invention, an 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.

[0013] 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 described above;
C) loading the printer with an ink jet ink composition; and
D) printing on the ink jet recording element using the ink jet ink

composition in response to the digital data signals.

[0014] In a preferred embodiment of the invention, the stabilizer complex described above is located in the image-receiving layer. In another preferred embodiment, M in the above formula is a Group IIIA, IIIB, IVA, IVB metal or a lanthanide group metal of the periodic chart, such as tin, titanium, zirconium, aluminum, silica, yttrium, cerium or lanthanum or mixtures thereof. In another preferred embodiment, the stabilizer described above is in a particulate form or is in an amorphous form. In another preferred embodiment, n is 4; a, b and c each comprise a rational number as follows: $0 \leq a < 1$; $1 < b < 4$; and $1 \leq pc < 4$, so that the charge of the M^{4+} metal ion is balanced. In still another preferred embodiment, a is 0, n is 4, and b+pc is 4. In yet still another preferred embodiment, a is 0, n is 3, and b+pc is 3.

[0015] In yet still another preferred embodiment of the invention, A^{p-} is an organic anion such as R-COO$^-$, R-O$^-$, R-SO_3-, R-OSO_3^- or R-O-PO_3^- where R is an alkyl or aryl group. In another preferred embodiment, A^{P-} is an inorganic anionic such as I^-, Cl^-, Br^-, F^-, ClO_4^-, NO_3^-, CO_3^{2-} or SO_4^{2-}. The particle size of the complex described above is less than 1 μm, preferably less than 0.1 μm.

[0016] Metal (oxy)hydroxide complexes employed herein may be prepared by dissolving a metal salt in water and adjusting the concentration, pH, time and temperature to induce the precipitation of metal (oxy)hydroxide tetramers, polymers or particulates. The conditions for precipitation vary depending upon the nature and concentrations of the counter ion(s) present and can be determined by one skilled in the art. For example, soluble complexes suitable for preparation of the zirconium (oxy)hydroxide particulates include, but are not limited to, $ZrOCl_2 \cdot 8H_2O$, and the halide, nitrate, acetate, sulfate, carbonate, propionate, acetylacetonate, citrate and benzoate salts; and hydroxy salts with any of the above anions. It is also possible to prepare the complexes employed in the invention via the hydrolysis of organically soluble zirconium complexes such as zirconium alkoxides, e.g., zirconium propoxide, zirconium isopropoxide, zirconium ethoxide and related organometallic zirconium compounds.

[0017] The hydrolyzed zirconium oxyhydroxides,

$$Zr(O)_a(OH)_b(AP^-)_c{}^*xH_2O$$

may exist as tetrameric zirconia units or as polymeric complexes of tetrameric zirconia, wherein zirconium cations are bridged by hydroxy and/or oxo groups. In general, hydrolyzed zirconia salts are amorphous and may exist predominantly in the α form. However, depending upon the experimental conditions (solvents, pH, additives, aging and heating conditions), the hydrolyzed product may contain significant number of "oxo" bridges.

[0018] It is often difficult to ascertain the precise composition of "oxo" and "hydroxy" groups in hydrolyzed metal salts. Therefore, the usage of definitive numbers for these functional groups in metal (oxy)hydroxide compositions was avoided. Any number of oligomeric or polymeric units of metal complexes may be condensed via hydrolysis reactions to form larger particulates ranging in size from 3 nm to 500 nm.

[0019] It is further possible to age or heat treat suspensions of the complexes to obtain particulates ranging in size from 0.500 μm to 5.0 μm. Preferred particles sizes are in the range from 5 nm to 1000 nm. Calcination of amorphous metal (oxy)hydroxide leads to the formation of crystalline polymorphs of metal oxides.

[0020] In a preferred embodiment of the invention, the image-receiving layer is porous and also contains a polymeric binder 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, rhamsan and the like. In still another preferred embodiment of the invention, the hydrophilic polymer is poly (vinyl alcohol), hydroxypropyl cellulose, hydroxypropyl methyl cellulose, or a poly(alkylene oxide). In yet still another preferred embodiment, the hydrophilic binder is poly(vinyl alcohol).

[0021] 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 particles, polymeric binder and/or crosslinker.

[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] 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.

[0027] 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 inorganic or organic particles, 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 elements are described in MCCUTCHEON's Volume 1: Emulsifiers and Detergents, 1995, North American Edition.

[0028] The ink receiving layer employed in the invention can contain one or more mordanting species or polymers. The mordant polymer can be a soluble polymer, a charged molecule, or a crosslinked dispersed microparticle. The mordant can be non-ionic, cationic or anionic.

[0029] 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.

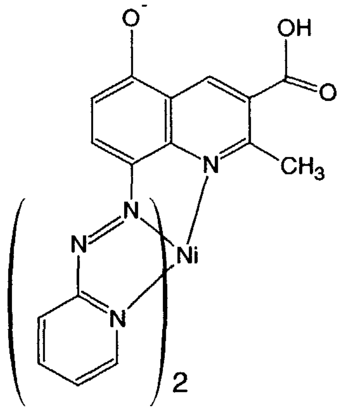
[0030] Ink jet inks used to image the recording elements of the present invention are well-known in the art. The ink compositions used in ink jet printing typically are liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, 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 watersoluble 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.

[0031] The following examples are provided to illustrate the invention.

<u>Example 1</u>

<u>Dye Stability Evaluation Tests</u>

[0032] The dye used for testing was a magenta colored ink jet dye having the structure shown below. To assess dye stability on a given substrate, a measured amount of the ink jet dye and solid particulates or aqueous colloidal dispersions of solid particulates (typically 10%-20.0% by weight solids) were added to a known amount of water such that the concentration of the dye was 10^{-5} M. The solid dispersions containing dyes were carefully stirred and then spin coated onto a glass substrate at a speed of 1000-2000 rev/min. The spin coatings obtained were left in ambient atmosphere with fluorescent room lighting (0.5 K1ux) kept on at all times during the measurement. The fade time was estimated by noting the time required for complete disappearance of magenta color as observed by the naked eye or by noting the time required for the optical absorption to decay to less than 0.03 of the original value.



Magenta Dye

Comparative Coatings C-1 to C-13 (Non-metal(oxy)hydroxide salts)

[0033] Inorganic particles of Al_2O_3, SiO_2, TiO_2, ZnO, MgO, ZrO_2, Y_2O_3, CeO_2, $CaCO_3$, $BaS0_4$, $Zn(OH)_2$, laponite and montmorillonite were purchased from commercial sources as fine particles or as colloidal particulate dispersions and were used to evaluate the stability of ink jet dyes in comparison with the materials employed in the present invention. The compositions and chemical identity of the samples was confirmed using powder X-ray diffraction techniques. The particulates were then coated and tested as described above.

Inventive Coatings I-1 to I-16

[0034] I-I. To a 5.0 g of 1M solution of $Al(NO_3)_3$•$6H_2O$, 6.3 g of an approximately 2.9% aqueous ammonia solution was added at room temperature with stirring. The resultant colloidal dispersion with pH about 5.5 was then coated and tested as described above and the results shown in Table 1 below.

[0035] I-2. To a 4.8 g of 1M solution of $AlCl_3$•$6H_2O$, 10.2 g of a 1 M sodium hydroxide was added at room temperature with stirring. The resultant colloidal dispersion with pH = 4.7 was then coated and tested as described above and the results shown in Table 1 below.

[0036] I-3. To a 5.0 g of 0.25 M solution of $CeCl_3$, 2.4 ml of a 0.2M sodium hydroxide was added at room temperature with stirring. The resultant colloidal dispersion with pH = 7.3 was then coated and tested as described above and the results shown in Table 1 below.

[0037] I-4. To a 5.0 g of 0.25 M solution of $Ce(CH_3COO)_3$•H_2O, 1.1 ml of a 0.2M sodium hydroxide was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.5 was then coated and tested as described above and the results shown in Table 1 below.

[0038] I-5. To a 5.0 g of 0.5 M solution of $Ce(NO_3)_3$•xH_2O, 0.8 ml of a 0.2M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.0 was then coated and tested as described above and the results shown in Table 1 below.

[0039] I-6. To a 5.0 g of 0.25 M solution of $La(CH_3COO)_3$•xH_2O, 0.12 ml of a 0.2M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.6 was then coated and tested as described above and the results shown in Table 1 below.

[0040] I-7. To a 5.0 g of 0.5 M solution of $La(NO_3)_3$•xH_2O, 0.8 ml of a 0.2M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.7 was then coated and tested as described above and the results shown in Table 1 below.

[0041] I-8. To a 5.0 g of 0.5 M solution of YCl_3•$6H_2O$, 0.7 ml of a 2.8-3.0% ammonia solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 6.6 was then coated and tested as described above and the results shown in Table 1 below.

[0042] I-9. To a 5.0 g of 0.5 M solution of $Y(NO)_3$•$6H_2O$, 3.1 ml of a 0.1 M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 6.4 was then coated and tested as described above and the results shown in Table 1 below.

[0043] I-10. To a 5.0 g of 0.25 M solution of $Y(CH_3COO)_3$•xH_2O, 1.5 ml of a 2.8-3.0% solution of ammonia hydroxide was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 9.6 was then coated and tested as described above and the results shown in Table 1 below.

[0044] I-11. To a 5.0 g of 0.25 M solution of $Gd(CH_3COO)_3 \cdot xH_2O$, 3.5 ml of a 0.2M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.5 was then coated and tested as described above and the results shown in Table 1 below.

[0045] I-12. To a 5.0 g of 0.25 M solution of $Sm(CH_3COO)_3 \cdot xH_2O$, 3.7 ml of a 0.2M sodium hydroxide solution was added slowly at room temperature, while stirring the reaction mixture. The resultant colloidal dispersion with pH = 7.5 was then coated and tested as described above and the results shown in Table 1 below.

[0046] I-13. A 10% colloidal dispersion of zirconium(iv)acetate hydroxide was made by adding 1.0 g of the salt in 9 ml of distilled water at room temperature. The resultant dispersion with pH *ca.* 4.1 was then coated and tested as described above and the results shown in Table 1 below.

[0047] I-14. To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 8.3 ml oflM sodium acetate was gradually added and vigorously stirred at room temperature. The final colloidal dispersion with *(ca.* 14% solids) pH *ca.* 3.0 was then coated and tested as described above and the results shown in Table 1 below.

[0048] I-15. To a 10.0 ml solution of 0.5 M $ZrOCl_2.8H_2O$, 1.7 ml of 0.5 M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion *(ca.* 19% solids) with pH 3.6 was then coated and tested as described above and the results shown in Table 1 below.

[0049] I-16. To a 5.0 ml of 20% solution of $Si(CH_3COO)_4$, 4.6 ml of 1M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 4.8 was then coated and tested as described above and the results shown in Table 1 below.

Table 1

Coating	Particle	Fade Time	Hue Change
C-1	Al_2O_3	18 hours	No
C-2	SiO_2	18 hours	No
C-3	TiO_2	18 hours	No
C-4	ZnO	2 days	No
C-S	MgO	18 hours	No
C-6	ZrO_2	18 hours	No
C-7	Y_2O_3	7 days	No
C-8	CeO_2	7 days	No
C-9	$CaCO_3$	5 days	Yes
C-10	$BaSO_4$	6 days	Yes
C-11	$Zn(OH)_2$	5 days	Yes
C-12	Laponite	4 days	No
C-13	Montmorillonite	18 hours	Yes
I-1	$Al(O)_a(OH)_b(NO_3)_c \cdot xH_2O$	> 30 days	No
I-2	$Al(O)_a(OH)_b(Cl)_c \cdot xH_2O$	> 30 days	No
I-3	$Ce(O)_a(OH)_b(Cl)_c \cdot xH_2O$	> 30 days	No
I-4	$Ce(O)_a(OH)_b(CH_3COO)_c \cdot x\ H_2O$	> 30 days	No
I-5	$Ce(O)_a(OH)_b(NO_3)_c \cdot xH_2O$	> 30 days	No
I-6	$La(O)_a(OH)_b(CH_3COO)_c \cdot x\ H_2O$	> 30 days	No
I-7	$La(O)_a(OH)_b(NO_3)_c \cdot x\ H_2O$	> 30 days	No
I-8	$Y(O)_a(OH)_b(Cl)_c \cdot x\ H_2O$	> 30 days	No
I-9	$Y(O)_a(OH)_b(NO_3)_c \cdot x\ H_2O$	> 30 days	No
I-10	$Y(O)_a(OH)_b(CH_3COO)_c \cdot x\ H_2O$	> 30 days	No
I-11	$Gd(O)_a(OH)_b(CH_3COO)_c \cdot x\ H_2O$	> 30 days	No
I-12	$Sm(O)_a(OH)_b(CH_3COO)_c \cdot x\ H_2O$	> 30 days	No

Table 1 (continued)

Coating	Particle	Fade Time	Hue Change
I- 13	$Zr(OH)_b(CH_3COO)_c(H_2O$, b+c=4	> 30 days	No
I-14	$Zr(O)_a(OH)_b(CH_3CH_2COO)_{0.83}$•$(Cl)_{1.17}H_2O$	> 30 days	No
I-15	$Zr(O)_a(OH)_b(Cl)_{1.83}H_2O$	> 30 days	No
I-16	$Si(O)_a(OH)_b(CH_3COO)_c$•xH_2O	> 30 days	No

[0050] The above results show that the complexes employed in the present invention provide superior image stability and stabilize the ink jet dye against fade and hue changes, particularly when compared to the control materials. The above results further show that the materials employed in the present invention can be prepared from various three and four valent metal ions, and from an assortment of inorganic and organic anions.

Example 2

[0051] Coatings were made and tested as in Example 1 using the materials described below. The results are shown in Table 2 below.

Comparative Coatings C-14 to C-18 (Non-metal(oxy)hydroxide salts)

[0052] Metal oxides, Al_2O_3, SiO_2, TiO_2, ZnO and ZrO_2, were purchased from commercial sources as nanoparticulate colloidal dispersions and were used to evaluate the stability of ink jet dyes in comparison with zirconium (oxy)hydroxides employed in the present invention. The particle size of the commercial colloids was typically in the range from 50 -500 nm. The pH of the colloids varied as shown in Table 2 below.

Inventive Coatings I-17 to I-37

[0053] I-17: $Zr(OH)_b(CH_3COO)_c$: A 10% solution of zirconium(iv)acetate hydroxide was made by dissolving 1.0 g of the salt in 9 ml of distilled water at room temperature. The final dispersion with pH *ca.* 4.1 was used for evaluating the stability of ink jet dyes as described above.

[0054] I-18. The composition of OH groups in I-17 was increased by the addition of 0.7 ml of 0.5 M NaOH to 10 ml of 10% I-17. The final dispersion with pH *ca.* 6.7 was used for evaluating the stability of ink jet dyes as described above.

[0055] I-19: The composition of OH groups in I-17 was farther increased by the addition of 1.1 ml of 0.5 M NaOH to 10 ml of 10% I- 17. The final dispersion with pH *ca.* 9.0 was used for evaluating the stability of ink jet dyes as described above.

[0056] I-20: In order to enhance the composition of acetate groups in I-17 (i.e. with lower pH), zirconium acetate solution *(ca.* 16%) in dilute acetic acid with pH 3.0 was used to evaluate the stability of ink jet dyes as described above.

[0057] I-21: $Zr(O)_a(OH)_b(CH_3COO)_{0.83}$•$(Cl)_{1.17}$•$xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 8.3 ml of 1M sodium acetate was gradually added and vigorously stirred at room temperature. The final colloidal dispersion with pH *ca.* 3.0 was used for evaluating the stability of the ink jet dyes as described above.

[0058] I-22: $Zr(O)_a(OH)_b(CH_3COO)$•(Cl)•xH_2O: To a 10.0 ml solution of 1M $ZrOCl_2.8H_20$, 10.0 ml of 1M sodium acetate was gradually added and vigorously stirred at room temperature. The final colloidal dispersion with pH around 4.0 was used for evaluating the stability of the ink jet dyes as described above.

[0059] I-23: $Zr(O)_a(OH)_b(CH_3COO)_{2.5}$•$xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 25.0 ml of 1M sodium acetate was gradually added while vigorously stirring at room temperature. The resultant thick gel like colloidal dispersion with pH 5.5 was used for evaluating the stability of the ink jet dyes as described above.

[0060] I-24: $Zr(O)_a(OH)_b(CH_3CH_2COO)_{1.5}$•$(Cl)_{0.5}$•$xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 15.0 ml of 1M sodium propionate was gradually added, while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 3.25 was used for evaluating the stability of the ink jet dyes as described above.

[0061] I-25: $Zr(O)_a(OH)_b(CH_3CH_2COO)_{3.0}$•$xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 30.0 ml of 1M sodium propionate was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 5.2 was used for evaluating the stability of the ink jet dyes as described above. A small amount of chloride anions may also bind to zirconium (oxy)hydroxides.

[0062] I-26: $Zr(O)_a(OH)_b(C_6H_5COO)_{1.75}$•$(Cl)_{0.25}$•$xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 35.0 ml of 0.5 M sodium benzoate was gradually added, while vigorously stirring at room temperature. The resultant thick gel like colloidal dispersion with pH 3.3 was used for evaluating the stability of the ink jet dyes as described above.

[0063] I-27: $Zr(O)_a(OH)_b(C_6H_5COO)_{2.5}•xH_2O$: To a 10.0 ml solution of 1M $ZrOCl_2.8H_2O$, 50.0 ml of 0.5 M sodium benzoate was gradually added while vigorously stirring at room temperature. The resultant thick gel like colloidal dispersion with pH 5.4 was used for evaluating the stability of the ink jet dyes as described above. A small amount of chloride anions may also bind to zirconium (oxy)hydroxides.

[0064] I-28: $Zr(O)_a(OH)_b(Cl)_{1.83}•xH_2O$: To a 10.0 ml solution of 0.5 M $ZrOCl_2.8H_2O$, 1.7 ml of 0.5 M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 3.6 was used for evaluating the stability of the ink jet dyes as described above.

[0065] I-29: $Zr(O)_a(OH)_b(Cl)_{1.79}•xH_2O$: To a 10.0 ml solution of 0.5 M $ZrOCl_2.8H_2O$, 2.1 ml of 0.5 M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 6.1 was used for evaluating the stability of the ink jet dyes as described above.

[0066] I-30: $Zr(O)_a(OH)_b(Cl)_c•xH_2O$: To a 10.0 ml solution of 0.5 M $ZrOCl_2.8H_2O$, 5.0 ml of 0.5 M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 12.9 was used for evaluating the stability of the ink jet dyes as described above. Above pH 7.0, the composition of OH groups in zirconium complexes may dominate due to base hydrolysis and a small percentage of chloride anions may bind to zirconium (oxy)hydroxides.

[0067] I-31: $Zr(O)_a(OH)_b(CO_3)_{0.7}(Cl)_{1.3}•xH_2O$: To a 10.0 ml solution of 1 M $ZrOCl_2.8H_2O$, 7.0 ml of 1 M sodium carbonate was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 3.4 was used for evaluating the stability of the ink jet dyes as described above.

[0068] I-32: $Zr(O)_a(OH)_b(CO_3)_c(Cl)d•xH_2O$: To a 10.0 ml solution of 1 M $ZrOCl_2.8H_2O$, 15.0 ml of 1 M sodium carbonate was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 7.7 was used for evaluating the stability of the ink jet dyes as described above. Above pH 7.0, the composition of OH groups in zirconium complexes may dominate due to base hydrolysis and a small percentage of "carbonate" and "chloride" anions may bind to zirconium (oxy)hydroxides.

[0069] I-33: $Zr(O)_a(OH)_b(NO_3)_{1.87}•xH_2O$: To a 10.0 ml solution of 0.5 M $ZrO(NO_3)_2.xH_2O$, 1.3 ml of 0.5 M sodium hydroxide was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 3.0 was used for evaluating the stability of the ink jet dyes as described above.

[0070] I-34: $Zr(O)_a(OH)_b(NO_3)_c•nH_2O$: To a 10.0 ml solution of 0.5 M $ZrO(NO_3)_2.xH_2O$, 2.2 ml of 0.5 M NaOH was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 11.3 was used for evaluating the stability of the ink jet dyes as described above. Above pH 7.0, the composition of OH groups in zirconium complexes may dominate due to base hydrolysis and a small percentage of nitrate anions may bind to the polycationic complexes of zirconium (oxy)hydroxides.

[0071] I-35: $Zr(O)_a(OH)_b(NO_3)_{1.52}(CO_3)_{0.48}•nH_2O$: To a 10.0 ml solution of 0.5 M $ZrO(NO_3)_2.xH_2O$, 2.4 ml of 1 M sodium carbonate was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 3.1 was used for evaluating the stability of the ink jet dyes as described above.

[0072] I-36: $Zr(O)_a(OH)_b(NO_3)_c(CO_3)_d•nH_2O$: To a 10.0 ml solution of 0.5 M $ZrO(NO_3)_2.xH_2O$, 6.0 ml of 1 M sodium carbonate was gradually added while vigorously stirring at room temperature. The resultant colloidal dispersion with pH 9.2 was used for evaluating the stability of the ink jet dyes as described above.

[0073] I-37: $Zr(OH)_4$: A 10% solution of zirconium(iv)hydroxide was made by dissolving 1.0 g of $Zr(OH)_4$ in 9 ml of distilled water at room temperature. The resultant solution with pH 7.9 was used for evaluating the stability of the ink jet dyes as described above.

Table 2

Coating	Particle	Fade Time	Hue Change
C-14	Al_2O_3	18 hours	No
C-15	ZrO_2	24 hours	No
C-16	SiO_2	18 hours	No
C-17	ZnO	2 days	No
C-18	TiO_2	18 hours	No
I-17	$Zr(OH)_b(CH_3COO)_c•xH_2O$, b+c=4	> 30 days	No
I-18	$Zr(OH)_b(CH_3COO)_c•xH_2O$, b+c=4, b > c	> 30 days	No
I-19	$Zr(OH)_b(CH_3COO)_c•xH_2O$, b+c =4, b >> c	> 30 days	Yes
I-20	$Zr(OH)_b(CH_3COO)_c•xH_2O$, b+c =4, b < c	> 30 days	No
I-21	$Zr(O)_a(OH)_b(CH_3COO)_{0.83}•(Cl)_{1.17}•xH_2O$	> 30 days	No

Table 2 (continued)

Coating	Particle	Fade Time	Hue Change
I-22	$Zr(O)_a(OH)_b(CH_3COO)\bullet(Cl)\bullet xH_2O$	> 30 days	No
I237	$Zr(O)_a(OH)_b(CH_3COO)_{2.5}\bullet xH_2O$	> 30 days	No
I-24	$Zr(O)_a(OH)_b(CH_3CH_2COO_{1.5}\bullet(Cl)_{0.5}\bullet xH_2O$	> 30 days	No
I-25	$Zr(O)_a(OH)_b(CH_3CH_2COO)_{3.0}\bullet xH_2O$	> 30 days	No
I-26	$Zr(O)_a(OH)_b(C_6H_5COO)_{1.75}\bullet(Cl)_{0.25}\bullet xH_2O$	> 25 days	No
I-27	$Zr(O)_a(OH)_b(C_6H_5COO)_{2.5}\bullet xH_2O$	> 25 days	No
I-28	$Zr(O)_a(OH)_b(Cl)_{1.83}\bullet xH_2O$	> 30 days	No
I-29	$Zr(O)_a(OH)_b(Cl)_{1.79}\bullet xH_2O$	> 30 days	No
I-30	$Zr(O)a(OH)_b(Cl)_c\bullet xH_2O$	> 30 days	Yes
I-31	$Zr(O)_a(OH)_b(CO_3)_{0.7}(Cl)_{1.3}\bullet xH_2O$	> 30 days	No
I-32	$Zr(0)_a(0H)_b(CO_3)_c(Cl)_d\bullet xH_2O$	> 30 days	Yes
I-33	$Zr(0)_a(OH)_b(NO_3)_{1.87}\bullet xH_2O$	> 30 days	No
I-34	$Zr(O)_a(OH)_b(NO_3)_c\bullet xH_2O$	> 30 days	Yes
I-35	$Zr(O)_a(OH)_b(NO_3)_{1.52}(CO_3)_{0.48}\bullet xH_2O$	> 30 days	No
I-36	$Zr(O)_a(OH)_b(NO_3)_c(CO_3)_d\bullet xH_2O$	> 30 days	Yes
I-37	$Zr(OH)_4.xH_2O$	12 days	Yes

[0074] The above results show that the anion stabilized, complex zirconium oxyhydroxide particulates employed in the invention provide considerable stability for a magenta ink jet dye when compared with the control materials. The data further show that the materials of the current invention are superior to "hydrous" zirconia, $Zr(OH)_4xH_2O$, in imparting stability to ink jet dyes.

Example 3

Element 1

[0075] A coating composition was prepared from 72.0 wt. % of a 20 wt. % solids aqueous colloidal suspension of zirconia (oxy)hydroxides stabilized by nitrate (Zrl 00/20 purchased from Nyacol® Nano Technologies, Inc), 3.6 wt. % poly(vinyl alcohol) (PVA) (Airvol 203 ® from Air Products), and 24.4 wt. % water. (The relative proportion of zirconia to PVA is therefore 80/20 by weight). The solution was coated onto a base support comprised of a polyethylene resin coated photographic paper stock, which had been previously subjected to corona discharge treatment, using a calibrated coating knife, and dried to remove substantially all solvent components to form the ink receiving layer.

Element 2

[0076] This element was prepared the same as Element 1 except that the coating composition was 74.0 wt. % of an aqueous colloidal suspension of zirconium (oxy)hydroxide stabilized by acetate (20 wt. % from Alfa Aesar, 0.005-0.01 micron particles, powder X-ray diffraction analysis indicated that the suspension contained an amorphous particulate.), 2.2 wt. % poly(vinyl alcohol) (Gohsenol® GH-17 from Nippon Gohsei Co.), and 23.8 wt. % water. (The relative proportion of zirconia to PVA is therefore 87/13 by weight).

Comparative Element C-1

[0077] This element was prepared the same as Element 1 except that the coating composition was 53.3 wt. % of a fumed Zirconia (a 30 wt. % aqueous suspension from Degussa, lot # 007-80, ID # 1TM106, powder X-ray diffraction analysis indicated that the suspension contained a crystalline ZrO_2 particulates), 4.0 wt. % poly(vinyl alcohol) (Airvol 203® from Air Products), and 42.7 wt. % water. (The relative proportion of zirconia to PVA is therefore 80/20 by weight).

Comparative Element C-2

[0078] This element was prepared the same as Element 1 except that the coating composition was 60.0 wt. % of silica (a 40 wt. % aqueous colloidal suspension ofNalco2329® (75 nm silicon dioxide particles) from Nalco Chemical Co.), 6.0 wt. % poly(vinyl alcohol) (Airvol 203® from Air Products), and 34.0 wt. % water. (The relative proportion of silica to PVA is therefore 80/20 by weigh).

Comparative Element C-3

[0079] This element was prepared the same as Element 1 except that the coating composition was 60.0 wt. % of a fumed alumina solution (40 wt. % alumina in water, Cab-O-Sperse® PG003 from Cabot Corporation), 6.0 wt. % poly (vinyl alcohol) (Airvol 203® from Air Products), and 34.0 wt. % water. (The relative proportion of alumina to PVA is therefore 80/20 by weight).

Comparative Element C-4

[0080] This element was prepared the same as Element 1 except that the coating composition was 64.0 wt. % of silica (a 40 wt. % aqueous colloidal suspension ofNalco2329® (75 nm silicon dioxide particles) from Nalco Chemical Co.), 4.5 wt. % poly(vinyl alcohol) (Airvol 203® from Air Products), and 31.5 wt. % water. (The relative proportion of silica to PVA is therefore 85/15 by weight.

Comparative Element C-5

[0081] This element was prepared the same as Element 1 except that the coating composition was 31.9 wt. % of silica (a 40 wt. % aqueous colloidal suspension of Nalco2329®(75 nm silicon dioxide particles) from Nalco Chemical Co.), 2.25 wt. % poly(vinyl alcohol) (Gohsenol® GH-17 from Nippon Gohsei Co.), and 65.85wt. % water. (The relative proportion of silica to PVA is therefore 85/15 by weight).

Printing and dye stability testing

[0082] The above elements were printed using a Lexmark Z51 ink jet printer and a cyan ink jet ink, prepared using a standard formulation with a copper phthalocyanine dye (Clariant Direct Turquoise Blue FRL-SF), and a magenta ink, prepared using a standard formulation with Dye 6 from U.S. Patent 6,001,161, as illustrated above. The red channel density (cyan) patches and green channel density (magenta) patches at D-max (the highest density setting) were read using an X-Rite ® 820 densitometer. The printed elements were then subjected to 4 days exposure to a nitrogen flow containing 5 ppm ozone. The density of each patch was read after the exposure test using an X-Rite ® 820 densitometer. The % dye retention was calculated as the ratio of the density after the exposure test to the density before the exposure test. The results for cyan and magenta D-max are reported in Table 3.

Table 3

Element	Material	% dye retention magenta D-max	% dye retention cyan D-max
1	Amorphous $ZrO(OH)NO_3$	100	92
2	Amorphous ZrO(OH)acetate	96	100
C-1	Crystalline ZrO_2	14	68
C-2	Silica	5	82
C-3	Alumina	5	57
C-4	Silica	3	64
C-5	alumina	6	88

[0083] The above results show that with a porous layer containing particulate complex zirconium oxyhydroxides, dye stability towards environmental gases is excellent, however, with a porous layer comprising crystalline zirconia or fine-particle silica or fine particle alumina, dye stability towards environmental gases such as ozone remains poor.

Claims

1. An ink jet recording element comprising a support having thereon an image-receiving layer, said ink jet recording element containing a metal(oxy)hydroxide complex,

$$M^{n+}(O)_a(OH)_b(A^{p-})_c \bullet xH_2O,$$

wherein
M is at least one metal ion;
n is 3 or 4;
A is an organic or inorganic ion;
p is 1, 2 or 3; and
x is equal to or greater than 0;
with the proviso that when n is 3, then a, b and c each comprise a rational number as follows: $0 \leq a < 1.5$; $0 < b < 3$; and $0 \leq pc < 3$, so that the charge of the M^{3+} metal ion is balanced;
and when n is 4, then a, b and c each comprise a rational number as follows: $0 \leq a < 2$; $0 < b < 4$; and $0 \lneqq pc < 4$, so that the charge of the M^{4+} metal ion is balanced.

2. The recording element of Claim 1 wherein said complex is present in said image-receiving layer.

3. The recording element of Claim 1 wherein M is a Group IIIA, IIIB, WA, IVB metal or a lanthanide group metal of the periodic chart.

4. The recording element of Claim 1 wherein M is tin, titanium, zirconium, aluminum, silica, yttrium, cerium or lanthanum or mixtures thereof.

5. The recording element of Claim 3 wherein A^{p-} is an organic anion R-COO-, R-O-, $R\text{-}SO_3^-$, $R\text{-}OSO_3^-$ or $R\text{-}O\text{-}PO_3^-$ where R is an alkyl or aryl group.

6. The recording element of Claim 1 wherein A^{p-} is an inorganic anion I-, Cl^-, Br^-, F^-, ClO_4^-, NO_3^-, CO_3^{2-} or SO_4^{2-}.

7. The recording element of Claim 1 wherein said metal(oxy)hydroxide complex is in particulate form.

8. The recording element of Claim 1 wherein said metal(oxy)hydroxide complex is prepared from an aqueous dispersion having a pH between 3 and 10.

9. The recording element of Claim 1 wherein M is Zr.

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 the ink jet recording element of Claim 1;
C) loading said printer with an ink jet ink composition; and
D) printing on said ink jet recording element using said ink jet ink composition in response to said digital data signals.