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

Tintenstrahlaufzeichnungselement und Druckverfahren

Elément d'enregistrement au jet d'encre et procédé d'impression

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(56) References cited:
EP-A- 0 914 961
EP-A- 1 167 056
DE-A- 19 709 735
US-A- 5 965 244

- **PATENT ABSTRACTS OF JAPAN vol. 1995, no. 08, 29 September 1995 (1995-09-29) & JP 7 137433 A (TOYOBO CO LTD), 30 May 1995 (1995-05-30)**

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Description

[0001] This invention relates to an ink jet recording element. More particularly, this invention relates to an ink jet recording element containing porous polymeric particles 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, 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-forming 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] While a wide variety of different types of image-recording elements for use with ink jet devices have been proposed heretofore, there are many unsolved problems in the art and many deficiencies in the known products which have limited their commercial usefulness.

[0005] It is well known that in order to achieve and maintain photographic-quality images on such an image-recording element, an ink jet recording element must:

- Be readily wetted so there is no puddling, i.e., coalescence of adjacent ink dots, which leads to non-uniform density
- Exhibit no image bleeding
- Absorb high concentrations of ink and dry quickly to avoid elements blocking together when stacked against subsequent prints or other surfaces
- Exhibit no discontinuities or defects due to interactions between the support and/or layer(s), such as cracking, repellencies, comb lines and the like
- Not allow unabsorbed dyes to aggregate at the free surface causing dye crystallization, which results in bloom or bronzing effects in the imaged areas
- Have an optimized image fastness to avoid fade from contact with water or radiation by daylight, tungsten light, or fluorescent light

[0006] An ink jet recording element that simultaneously provides an almost instantaneous ink dry time and good image quality is desirable. However, given the wide range of ink compositions and ink volumes that a recording element needs to accommodate, these requirements of ink jet recording media are difficult to achieve simultaneously.

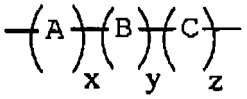
[0007] Ink jet recording elements are known that employ porous or non-porous single layer or multilayer coatings that act as suitable image-receiving layers on one or both sides of a porous or non-porous support. Recording elements that use non-porous coatings typically have good image quality but exhibit poor ink dry time. Recording elements that use porous coatings exhibit superior dry times, but typically have poorer image quality and are prone to cracking and flaking.

[0008] Japanese Kokai Hei 7[1995]-137433 relates to an ink jet recording paper containing polyester-based hollow porous resin particles containing cationic groups. However, it would be desirable to provide porous resin particles containing cationic groups which are not limited to polyester resins.

[0009] Japanese Kokai Hei 11 [1999]-8569 relates to an ink jet recording sheet comprising porous organic particles which may be made cationic by adsorbing a cationic surfactant. However, there is a problem with these particles in that the cationic functionality is not part of the polymeric structure and is only adsorbed to the surface, not chemically bound, so that it could be desorbed from the particle surface during manufacture, storage or imaging.

[0010] It is an object of this invention to provide an inkjet recording element that has a fast ink dry time. It is another object of this invention to provide an ink jet recording element containing porous particles which have an ionic functionality which will bind ink jet inks thereto, thereby providing a porous receiver that has good water fastness. It is another object of this invention to provide an ink jet recording element that has superior coating quality with acceptable cracking and flaking with low particle agglomeration. Still another object of the invention is to provide a printing method using the above described element.

[0011] These 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 comprising porous polymeric particles in a polymeric binder, the porous polymeric particles having the formula:



wherein:

A represents units of an addition polymerizable monomer containing at least two ethylenically unsaturated groups;
B represents units of copolymerizable monomers selected from the group consisting of acrylic monomers, nitriles and amides of acrylic acid or methacrylic acid, vinyl compounds, vinyl aromatic compounds, dialkyl esters, and mixtures thereof;
C represents styrenic or acrylic repeating units containing an ionic functionality;
x is from 27 to 99 mole %;
y is from 0 to 72 mole %; and
z is from 1 to 73 mole %.

[0012] By use of the invention, an ink jet recording element is obtained which has better dry time, water fastness and coating quality (cracking and flaking) than prior art elements while providing good image quality.

[0013] In a preferred embodiment of the invention, x is from 55 to 99 mole %; y is from 0 to 44 mole %; and z is from 1 to 45 mole %.

[0014] 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 the printer with an ink jet ink composition; and
D) printing on the image-receiving layer using the ink jet ink composition in response to the digital data signals.

[0015] The support used in the ink jet recording element of the invention may be opaque, translucent or transparent. There may be used, for example, plain papers, resin-coated papers, plastics including a polyester resin such as poly (ethylene terephthalate), poly(ethylene naphthalate) and poly(ester diacetate), a polycarbonate resin, a fluorine resin such as poly(tetra-fluoro ethylene), metal foil, various glass materials, various voided or filled opaque plastics and the like. In a preferred embodiment, the support is paper or a voided plastic material. The thickness of the support employed in the invention can be from 12 to 500 μm, preferably from 75 to 300 μm.

[0016] The porous polymeric particles which are used in the invention are in the form of porous beads, porous irregularly shaped particles, or are aggregates of emulsion particles and contain an ionic functionality.

[0017] Suitable addition polymerizable monomers which can be used as Unit A above contain at least two ethylenically unsaturated groups, and may include, for example, the following monomers and their mixtures: esters of unsaturated monohydric alcohols with unsaturated monocarboxylic acids, such as allyl methacrylate, allyl acrylate, butenyl acrylate, undecenyl acrylate, undecenyl methacrylate, vinyl acrylate, and vinyl methacrylate; dienes such as butadiene and isoprene; esters of saturated glycols or diols with unsaturated monocarboxylic acids, such as, ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,3-butanediol dimethacrylate, pentaerythritol tetraacrylate, trimethylol propane trimethacrylate and polyfunctional aromatic compounds such as divinylbenzene divinylnaphthalene or derivatives thereof or other divinyl compound such as divinyl sulfide or divinyl sulfone compound, and the like. Preferably, A includes ethylene glycol dimethacrylate, ethylene glycol diacrylate, 1,4-butanediol dimethylacrylate or divinylbenzene. Most preferably, A is divinylbenzene or ethylene glycol dimethacrylate.

[0018] Copolymerizable monomers which can be used as Unit B above are the following monomers and their mixtures: acrylic monomers, such as acrylic acid, or methacrylic acid, and their alkyl esters such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, n-octyl acrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, nonyl acrylate, benzyl methacrylate; the hydroxyalkyl esters of the same acids, such as, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, and 2-hydroxypropyl methacrylate; the nitriles and amides of the same acids, such as, acrylonitrile, methacrylonitrile, acrylamide, t-butylacrylamide and methacrylamide; vinyl compounds, such as, vinyl acetate, vinyl propionate, vinylidene chloride, vinyl chloride, and vinyl aromatic compounds such as styrene, t-butyl styrene, ethylvinylbenzene, chloromethylstyrene, vinyl toluene, styrene sulfonylchloride, vinylpyridine, and vinylimidazole; dialkyl esters, such as, dialkyl maleates, dialkyl itaconates, dialkyl methylene-malonates and the like. Preferably, B is styrene, vinyl toluene, ethylvinylbenzene, 2-hydroxyethyl methacrylate, chloromethylstyrene, methacrylic acid or methyl methacrylate.

[0019] The styrenic or acrylic repeating units of C above contain an ionic functionality which may be obtained using a preformed ionic monomer which carries a substantially permanent charge which survives the polymerization. Alternatively, functionalities in a formed porous polymeric particle can be modified to make them ionic. For example, pyridine can be protonated with an acid to form a quaternary nitrogen, an amine group can be quaternized with a chloroalkane, a carboxylic acid group can be neutralized with an amine or an alkali metal hydroxide to form a carboxylic anion, a chloromethyl group can be reacted with an amine to form a quaternary ammonium group, etc. Modifying functionalities in a formed porous polymeric particle is preferred.

[0020] Suitable copolymerizable, α, β-ethylenically unsaturated monomers containing a preformed ionic functionality which can be used as Unit C include, for example, the following monomers and their mixtures: cationic ethylenically unsaturated monomers, for example, vinylbenzyltrimethylammonium chloride, vinylbenzyldimethyl-dodecylammonium chloride, other vinylbenzylammonium salts in which the three other ligands on the nitrogen can be any alkyl or carbocyclic group including cyclic amines such as piperidine, the counter ions of which can be halides, sulfonates, phosphates, sulfates, etc.; [2-(methacryloyloxy)ethyl]trimethyl-ammonium chloride, [2-(acryloyloxy)ethyl]-trimethylammonium p-toluene-sulfonate, and other acrylate and methacrylate ammonium salts in which the alkyl group connecting the acrylic function to the nitrogen can be ≥ 2 carbon atoms long and the other three nitrogen ligands can be any alkyl or carbocyclic group including cyclic amines such as piperidine, and benzyl; 4-vinyl-1-methylpyridinium methyl sulfate, 3-methyl-1-vinylimidazolium methosulfate, and other vinylpyridinium and vinylimidazolium salts in which the other nitrogen ligand is any alkyl or cycloalkyl group; vinyltriphenyl-phosphonium bromide, vinylbenzyltriphenylphosphonium tosylate, and other phosphonium salts in which the other three phosphorous ligands are any aromatic or alkyl group. In a preferred embodiment, the cationic functionality is vinylbenzyltrimethylammonium chloride, vinylbenzyl-N-butylimidazolium chloride, vinylbenzyldimethyldodecylammonium chloride or vinylbenzyldimethyloctadecylammonium chloride.

[0021] Other suitable copolymerizable, α, β-ethylenically unsaturated monomers containing a preformed ionic functionality which can be used as Unit C include, for example, the following monomers and their mixtures: anionic ethylenically unsaturated monomers such as 2-phosphatoethyl acrylate potassium salt, 3-phosphatopropyl methacrylate ammonium salt, and other acrylic and methacrylic esters of alkylphosphonates in which the alkyl group connecting the acrylic function to the phosphate function can be ≥ 2 carbon atoms long, the counter ions of which can be alkali metal cations, quaternary ammonium cations, phosphonium cations, or the like; sodium methacrylate, potassium acrylate, and other salts of carboxylic acids; styrenesulfonic acid ammonium salt, methyltriphenylphosphonium styrenesulfonate, and other styrene sulfonic acid salts; 2-sulfoethyl methacrylate pyridinium salt, 3-sulfopropyl acrylate lithium salt, and other acrylic and methacrylic esters of alkylsulfonates; and other sulfonates such as ethylene sulfonic acid sodium salt. In a preferred embodiment, the anionic functionality is trimethylammonium salt of methacrylic acid, dimethylbenzylammonium salt of methacrylic acid, dimethyldodecylammonium salt of methacrylic acid or methyltrioctylammonium salt of styrenesulfonic acid.

[0022] If the repeating Unit C is to be formed after the porous polymeric particle is prepared, all or some of Units A or Units B in a porous polymeric particle can be modified to make them (or part of them) ionic. All of the cationic and anionic functionalities mentioned above can be incorporated by modifying a non-ionic porous polymeric particle.

[0023] The porous polymeric particles used in this invention can be prepared, for example, by pulverizing and classification of porous organic compounds, by emulsion, suspension, and dispersion polymerization of organic monomers, by spray drying of a solution containing organic compounds, or by a polymer suspension technique which consists of dissolving an organic material in a water immiscible solvent, dispersing the solution as fine liquid droplets in aqueous solution, and removing the solvent by evaporation or other suitable techniques. The bulk, emulsion, dispersion, and suspension polymerization procedures are well known to those skilled in the polymer art and are taught in such textbooks as G. Odian in "Principles of Polymerization", 2nd Ed. Wiley (1981), and W.P. Sorenson and T.W. Campbell in "Preparation Method of Polymer Chemistry", 2nd Ed, Wiley (1968).

[0024] Techniques to synthesize porous polymer particles are taught, for example, in U.S. Patents 5,840,293; 5,993,805; 5,403,870; and 5,599,889, and Japanese Kokai Hei 5[1993]-222108. For example, an inert fluid or porogen may be mixed with the monomers used in making the porous polymer particles. After polymerization is complete, the resulting polymeric particles are, at this point, substantially porous because the polymer has formed around the porogen thereby forming the pore network. This technique is described more fully in U.S. Patent 5,840,293 referred to above.

[0025] A preferred method of preparing the porous polymeric particles used in this invention includes forming a suspension or dispersion of ethylenically unsaturated monomer droplets containing the crosslinking monomer A, the monomer containing an ionic functionality or a monomer containing a group which will be converted to an ionic functionality, and a porogen in an aqueous medium, polymerizing the monomer to form porous polymeric particles, and optionally removing the porogen by vacuum stripping. In a preferred embodiment of the invention, the particles thus prepared have a porosity as measured by a specific surface area of greater than 100 m^2/g. The surface area is usually measured by B.E.T. nitrogen analysis known to those skilled in the art.

[0026] The porous polymeric particles used in the invention may be covered with a layer of colloidal inorganic particles as described in U.S. Patents 5,288,598; 5,378,577; 5,563,226 and 5,750,378. The porous polymeric particles may also be covered with a layer of colloidal polymer latex particles as described in U.S. Patent 5,279,934.

[0027] The porous polymeric particles used in this invention generally have a median diameter of from 0.05 μm to 10 μm, preferably from 0.1 μm to 5 μm. Median diameter is defined as the statistical average of the measured particle size distribution on a volume basis. For further details concerning median diameter measurement, see T. Allen, "Particle Size Measurement", 4th Ed., Chapman and Hall, (1990).

[0028] As noted above, the polymeric particles used in the invention are porous. By porous is meant particles which either have voids or are permeable to liquids. Preferred are particles which have voids. These particles can have either

a smooth or a rough surface.

[0029] The polymeric binder used in the invention may comprise a poly(vinyl alcohol), a gelatin, a cellulose ether, polyvinylpyrrolidone, poly(ethylene oxide), etc. In a preferred embodiment of the invention, the ratio of the particles to the binder is from 2:1 to 15:1.

[0030] The image-receiving layer may also contain additives such as pH-modifiers like nitric acid, cross-linkers, rheology modifiers, surfactants, UV-absorbers, biocides, lubricants, water-dispersible latexes, mordants, dyes, optical brighteners etc.

[0031] The image-receiving layer may be applied to one or both substrate surfaces through conventional pre-metered or post-metered coating methods such as blade, air knife, rod, roll, slot die, curtain, slide, etc. The choice of coating process would be determined from the economics of the operation and in turn, would determine the formulation specifications such as coating solids, coating viscosity, and coating speed.

[0032] The image-receiving layer thickness may range from 5 to 100 μm, preferably from 10 to 50 μm. The coating thickness required is determined through the need for the coating to act as a sump for absorption of ink solvent.

[0033] 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.

[0034] The following examples further illustrate the invention.

Preparation C1-Synthesis of Control Polymeric Particles (No ionic functionality)

[0035] To a beaker were added the following ingredients: 53 g methacrylic acid and 208 g ethylene glycol dimethacrylate as a monomer mixture, 132 g toluene as a porogen, 8 g hexadecane, and 3.9 g 2,2'-azobis(2,4-dimethylvaleronitrile), Vazo 52® (DuPont Corp.). The ingredients were stirred until all the solids were dissolved.

[0036] To this solution was added a mixture of 1.6 g alkyl (C_{14} 50%, C_{16} 10%, C_{12} 40%) dimethyl benzyl ammonium chloride, Barquat MB-50® (Lonza Inc.) in 1200 g water, which had been adjusted to pH=2.5 with 10% hydrochloric acid. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Gaulin® colloid mill set at 3600 rev./min., 0.25 mm gap, and 3.8 kg/minute throughput. The resulting monomer droplet dispersion was placed into a 2-liter three-necked round bottom flask. The flask was placed in a 50°C constant temperature bath and the dispersion stirred at 130 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. The product was filtered through a coarse filter to remove coagulum. Next, 0.6 g MAZU® antifoam agent (BASF Corp.) was added and toluene and some water were distilled off under vacuum at 60°C to give 28.9% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.5 μm in median diameter. The pH was measured and found to be 3.3. A dried portion of the dispersion, analyzed by B.E.T. Multipoint using a Quantachrome Corp., NOVA® analyzer had a specific surface area of 21 m^2/g.

Preparation 1- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0037] The dispersion described in Preparation C1 above was modified by reacting it with trimethylamine to form an ionic functionality. The pH was measured and found to be 6.9. The dispersion was determined to be 28.9% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.5 μm in median diameter.

Preparation 2- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0038] The dispersion described in Preparation C1 above was modified by reacting it with N, N-dimethyl-N-benzylamine to form an ionic functionality. The pH was measured and found to be 6.4. The dispersion was determined to be 29.7% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.5 μm in median diameter.

Preparation C2- Synthesis of Control Polymeric Particles (No ionic functionality)

[0039] To a beaker were added the following ingredients: 321.6 g divinylbenzene, DVB-HP® (Dow Chemical Corp.)

and 80.4 g methacrylic acid as a monomer mixture, 774 g toluene as a porogen, 24 g hexadecane, and 6.0 g 2,2'-azobis (2,4-dimethylvaleronitrile), Vazo 52®. The ingredients were stirred until all the solids were dissolved.

[0040] To this solution was added a mixture of 22.5 g sodium acetate trihydrate, 45.0 g acetic acid, 51.9 g of a low molecular weight copolymer of methylaminoethanol and adipic acid, and 624 g 50% colloidal silica, Ludox TM® (DuPont Corp.) in 2070 g water. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Gaulin® homogenizer at 240 kg/cm^2. The resulting monomer droplet dispersion was placed into a 5-liter three-necked round bottom flask. The flask was placed in a 50° constant temperature bath and the dispersion stirred at 125 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. The product was filtered through a coarse filter to remove coagulum. Next, toluene and some water were distilled off under vacuum at 60° to give 24.6% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.3 μm in median diameter. The pH was measured and found to be 4.3. A dried portion of the dispersion, analyzed by B.E.T. Multipoint using a Quantachrome Corp. NOVA® analyzer had a specific surface area of 221.98 m^2/g.

Preparation 3- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0041] The dispersion described in Preparation C2 above was modified by reacting it with 70.9 g N, N-dimethyl-N-dodecylamine to form an ionic functionality. The pH was measured and found to be 6.1. The dispersion was determined to be 26.4% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.7 μm in median diameter. A dried portion of the dispersion, analyzed by B.E.T. Multipoint using a Quantachrome Corp. NOVA® had a specific surface area of 137 m^2/g.

Preparation C3 - Synthesis of Control Polymeric Particles (No ionic functionality)

[0042] To a beaker were added the following ingredients: 134 g divinylbenzene, DVB-HP® as a monomer, 258 g toluene as a porogen, 8 g hexadecane, and 2.0 g 2,2'-azobis(2,4-dimethylvaleronitrile), Vazo 52®. The ingredients were stirred until all the solids were dissolved.

[0043] To this solution was added a mixture of 7.5 g sodium acetate trihydrate, 15.0 g acetic acid, 17.3 g of a low molecular weight copolymer of methylaminoethanol and adipic acid, and 208 g 50% silica, Ludox TM® in 690 g water. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Gaulin® homogenizer at 225 kg/cm^2. The resulting monomer droplet dispersion was placed into a 2-liter three-necked round bottom flask. The flask was placed in a 50° constant temperature bath and the dispersion stirred at 150 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. Toluene and some water were distilled off under vacuum at 60°C. The product was filtered through a coarse filter to remove coagulum to give a product of 23.4% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.0 μm in median diameter.

Preparation 4- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0044] To a beaker were added the following ingredients: 107.2 g divinylbenzene, DVB-HP® and 26.8 g chloromethylstyrene as a monomer mixture, 258 g toluene as a porogen, 8 g hexadecane, and 2.0 g 2,2'-azobis(2,4-dimethylvaleronitrile), Vazo 52®. The ingredients were stirred until all the solids were dissolved.

[0045] To this solution was added a mixture of 7.5 g sodium acetate trihydrate, 15.0 g acetic acid, 17.3 g of a low molecular weight copolymer of methylaminoethanol and adipic acid, and 208 g 50% silica, Ludox TM® in 690 g water. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Gaulin® homogenizer at 225 kg/cm^2. The resulting monomer droplet dispersion was placed into a 2-liter three-necked round bottom flask. The flask was placed in a 50°C constant temperature bath and the dispersion stirred at 150 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. Toluene and some water were distilled off under vacuum at 60°C. The product was filtered through a coarse filter to remove coagulum to give a product of 22.7% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.0 μm in median diameter.

[0046] Three 345 g aliquots of the above dispersion were put into three one-liter three-necked round bottomed flasks, each equipped with a paddle stirrer and condenser. Two of the aliquots were set aside for use in Preparations 5 and 6. Into the third aliquot was placed 50 mL of a 25 wt % solution of trimethylamine in water, and 250 g distilled water. The dispersion was stirred and heated overnight at 60°C. Unreacted trimethylamine was distilled off under vacuum at 60°C, and the pH was measured to be 7.5. The product was filtered through a coarse filter to remove coagulum. The final product was 12.4% solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.2 μm in median diameter. A dried portion of the dispersion, analyzed by B.E.T. Multipoint using a

Quantachrome Corp. NOVA® analyzer had a specific surface area of 165 m^2/g.

Preparation 5- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0047] Into one of the remaining three-necked round bottomed flasks containing 345 g of the dispersion from Preparation 4 was placed 11.2 g of N-butylimidazole and 300 g distilled water. The dispersion was stirred and heated overnight at 60°C. The product was filtered through a coarse filter to remove coagulum. The final product was 13.5% solids, pH=6.5. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.2 μm in median diameter.

Preparation 6- Porous Polymeric Particles Containing Ionic Functionality Invention

[0048] Into the remaining three-necked round bottomed flask containing 345 g of the dispersion from Preparation 4 was placed 19.2 g of dimethyldodecylamine and 250 g distilled water. The dispersion was stirred and heated overnight at 60°C. The product was filtered through a coarse filter to remove coagulum. The final product was 12.4% solids, pH=6.5. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 1.5 μm in median diameter.

Preparation 7- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0049] To a beaker were added the following ingredients: 107.2 g ethylene glycol dimethacrylate and 26.8 g N-vinylbenzyl-N,N-dimethyl-N-octadecylammonium chloride as a monomer mixture, 62 g propyl acetate as a porogen, 4 g hexadecane, and 2.25 g 2,2'-azobis(2,4-dimethylvaleronitrile), Vazo 52®. The ingredients were stirred until all the solids were dissolved.

[0050] To this solution was added a mixture of 0.8 g Barquat MB-50® in 600 g water. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Gaulin® colloid mill set at 3650 rev./min., 0.17 mm gap, and 3.8 kg/min throughput. The resulting monomer droplet dispersion was placed into a 2-liter three-necked round bottom flask. The flask was placed in a 50°C constant temperature bath and the dispersion stirred at 140 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. Propyl acetate and some water were distilled off under vacuum at 60°C. The product was filtered through a coarse filter to remove coagulum. The final product was 15.2 % solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 0.74 μm in median diameter.

Preparation 8- Porous Polymeric Particles Containing Ionic Functionality (Invention)

[0051] To a beaker were added the following ingredients: 234 g ethylene glycol dimethacrylate and 26 g methyltrioctylammonium styrenesulfonate as a monomer mixture, 132 g toluene as a porogen, 8 g hexadecane, and 3.9 g 2,2'-azobis(2,4-dimethylvaleronitrile), Vazo 52®. The ingredients were stirred until all the solids were dissolved.

[0052] To this solution was added a mixture of 24 g sodium dodecylbenzene sulfonate and 1200 g water. The mixture was then stirred with a marine prop type agitator for 5 minutes to form a crude emulsion. The crude emulsion was passed through a Crepaco® homogenizer at 420 kg/cm^2. The resulting monomer droplet dispersion was placed into a 2-liter three-necked round bottom flask. The flask was placed in a 50°C constant temperature bath and the dispersion stirred at 130 rev./min. under positive pressure nitrogen for 16 hours to polymerize the monomer droplets into porous polymeric particles. Toluene and some water were distilled off under vacuum at 60°C. The product was filtered through a coarse filter to remove coagulum. The final product was 13.5 % solids. The porous polymeric particles were measured by a particle size analyzer, Horiba LA-920®, and found to be 0.17 μm in median diameter.

Coating of Elements

Control Element C-1

[0053] A coating solution was prepared by mixing together the control porous polymeric particles of Preparation C1 with a binder of poly(vinyl alcohol) using Gohsenol GH 23® (Gohsen Nippon of Japan). The resulting coating solution was 15% solids and 85% water, with the solids being 85% porous polymeric particles and 15% poly(vinyl alcohol). The solution was stirred at 40°C for approximately 30 minutes before coating.

[0054] The solution was then coated on corona discharge-treated, photographic grade, polyethylene-coated paper using a wound wire metering rod, to a wet lay down of 120 μm, and oven dried for 30 minutes at 60°C. This element

was coated to a dry thickness of 18 μm.

Control Element C-2

[0055] This element was prepared the same as Control Element C-1 except that the coating solution was made using Preparation C2

Control Element C-3

[0056] This element was prepared the same as Control Element C-1 except that the coating solution was made using Preparation C3.

Elements 1-8 (Invention)

[0057] These elements were prepared the same as Control Element C-1 except that the coating solutions were made using Preparations 1-8, respectively.

Coating Quality Evaluation

[0058] Coating quality is a visual inspection of the above coated elements, looking at coating defects such as cracking, particle agglomeration, coating flaking off, coating uniformity or smoothness. The following evaluations in Table 1 were used and the results listed below in Table 3:

Table 1

Rating	Coating Defects
1	No cracks, no flakes, uniform coating
2	Very slight cracks, very slight particle agglomeration
3	Some cracks, no flaking, some particle agglomeration
4	Severe cracking, some flaking, heavy particle agglomeration
5	Major cracking, coating flaking off, heavy particle agglomeration
Ratings 1 and 2 are acceptable while ratings 3 to 5 are unacceptable.	

Water fastness Evaluation

[0059] Using an Epson 870 ink jet printer patches of cyan, magenta, yellow, and black were printed at 50% ink lay down. The images were dried for 24 hours. A 2-mil drop of distilled water was placed on each patch for 60 seconds and then rubbed off with a tissue. Damage to the image and the coating was visually observed and rated according to Table 2, with the results listed below in Table 3:

Table 2

Rating	Water Damage
1	No visual damage to image or coating
2	Slight image damage, "stained", no coating damage
3	Slight ink removal, imaged damaged, no coating damage
4	Heavy ink removal and image damage, some coating damage
5	Ink and coating removed, image removed
Ratings 1 to 3 are acceptable and ratings 4 to 5 are unacceptable.	

Evaluation of Elements

[0060] The above elements were evaluated as described above with the following results:

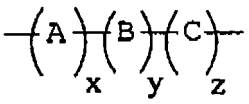
Table 3

Element	Coating Quality	Water fastness
Control C-1	2	5
1	1	3
2	1	3
Control C-2	2	5
3	1	2
Control C-3	2	4
4	1	2
5	1	2
6	2	2
7	2	2
8	1	2

[0061] The above results show that Control Elements C-1 to C-3 have unacceptable water fastness, while Inventive Elements 1 to 8 have acceptable coating quality and water fastness.

Claims

1. An ink jet recording element comprising a support having thereon an image-receiving layer comprising porous polymeric particles in a polymeric binder, the porous polymeric particles having the formula:



wherein:

A represents units of an addition polymerizable monomer containing at least two ethylenically unsaturated groups;
B represents units of copolymerizable monomers selected from the group consisting of acrylic monomers, nitriles and amides of acrylic acid or methacrylic acid, vinyl compounds, vinyl aromatic compounds, dialkyl esters, and mixtures thereof;
C represents styrenic or acrylic repeating units containing an ionic functionality;
x is from 27 to 99 mole %;
y is from 0 to 72 mole %; and
z is from 1 to 73 mole %.

2. The element of Claim 1 wherein said ionic functionality of said styrenic or acrylic repeating unit is cationic.

3. The element of Claim 2 wherein said cationic functionality is vinylbenzyltrimethylammonium chloride, vinylbenzyl-N-butylimidazolium chloride, vinylbenzyldimethyldodecylammonium chloride or vinylbenzyldimethyloctadecylam-

monium chloride.

4. The element of Claim 1 wherein said ionic functionality of said styrenic or acrylic repeating unit is anionic.

5. The element of Claim 4 wherein said anionic functionality is trimethylammonium salt of methacrylic acid, dimethylbenzylammonium salt of methacrylic acid, dimethyldodecylammonium salt of methacrylic acid or methyltrioctylammonium salt of styrenesulfonic acid.

6. The element of Claim 1 wherein
x is from 55 to 99 mole %;
y is from 0 to 44 mole %; and
z is from 1 to 45 mole %.

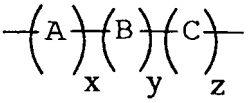
7. The element of Claim 1 wherein said porous polymeric particles have a median diameter of from 0.05 μm to 10 μm.

8. The element of Claim 1 wherein said porous polymeric particles have a median diameter of from 0.1 μm to 5 μm.

9. The element of Claim 1 wherein said polymeric binder comprises a poly(vinyl alcohol), a gelatin, a cellulose ether, poly(vinyl pyrrolidone) or poly(ethylene oxide).

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 comprising a support having thereon an image-receiving layer comprising porous polymeric particles in a polymeric binder, the porous polymeric particles having the formula:



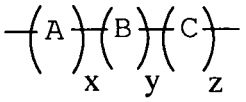
wherein:

A represents units of an addition polymerizable monomer containing at least two ethylenically unsaturated groups;
B represents units of copolymerizable monomers selected from the group consisting of acrylic monomers, nitriles and amides of acrylic acid or methacrylic acid, vinyl compounds, vinyl aromatic compounds, dialkyl esters, and mixtures thereof;
C represents styrenic or acrylic repeating units containing an ionic functionality;
x is from about 27 to about 99 mole %;
y is from 0 to about 72 mole %; and
z is from about 1 to about 73 mole %;

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.

Patentansprüche

1. Tintenstrahl-Aufzeichnungselement mit einem Träger, auf dem sich eine Bildempfangsschicht befindet, die poröse polymere Teilchen in einem polymeren Bindemittel umfasst, wobei die porösen polymeren Teilchen folgende Formel haben:



worin:

A Einheiten eines durch Additionspolymerisation polymerisierbaren Monomers darstellt, das mindestens zwei olefinisch ungesättigte Gruppen enthält;
B Einheiten von copolymerisierbaren Monomeren darstellt, die aus der aus Acrylmonomeren, Nitrilen und Amiden von Acrylsäure oder Methacrylsäure, Vinylverbindungen, aromatischen Vinylverbindungen, Dialkylestem bestehenden Gruppe und Gemischen davon ausgewählt wurden;
C styrolische oder acrylische wiederkehrende Einheiten darstellt, die eine ionische Funktionalität aufweisen;
x zwischen 27 und 99 Mol-%;
y zwischen 0 und 72 Mol-%; und
z zwischen 1 und 73 Mol-% liegt.

2. Element nach Anspruch 1, worin die ionischen Funktionalität der wiederkehrenden styrolischen oder acrylischen Einheiten kationisch ist.

3. Element nach Anspruch 2, worin es sich bei der kationischen Funktionalität um Vinylbenzyltrimethylammoniumchlorid, Vinylbenzyl-N-butylimidazoliumchlorid, Vinylbenzyldimethyldodecylammoniumchlorid oder Vinylbenzyldimethyloctadecylammoniumchlorid handelt.

4. Element nach Anspruch 1, worin die ionische Funktionalität der wiederkehrenden styrolischen oder acrylischen Einheiten anionisch ist.

5. Element nach Anspruch 4, worin es sich bei der anionischen Funktionalität um das Trimethylammoniumsalz der Methacrylsäure, das Dimethylbenzylammoniumsalz der Methacrylsäure, das Dimethyldodecylammoniumsalz der Methacrylsäure oder das Methyltrioctylammoniumsalz der Styrolsulfonsäure handelt.

6. Element nach Anspruch 1, worin
x zwischen 55 und 99 Mol-%;
y zwischen 0 und 44 Mol-%; und
z zwischen 1 und 45 Mol-% liegt.

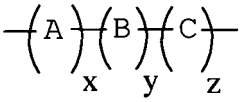
7. Element nach Anspruch 1, worin der Medianwert für den Durchmesser der porösen polymeren Teilchen zwischen 0,05 μm und 10 μm liegt.

8. Element nach Anspruch 1, worin der Medianwert für den Durchmesser der porösen polymeren Teilchen zwischen 0,1 μm und 5 μm liegt.

9. Element nach Anspruch 1, worin das polymere Bindemittel einen Polyvinylalkohol, eine Gelatine, einen Celluloseether, Polyvinylpyrrolidon oder Polyethylenoxid umfasst.

10. Tintenstrahldruckverfahren mit folgenden Schritten:

A) Bereitstellen eines Tintenstrahldruckers, der auf digitale Datensignale anspricht;
B) Beladen des Druckers mit einem Tintenstrahl-Aufzeichnungselement mit einem Träger, auf dem sich eine Bildempfangsschicht befindet, die poröse polymere Teilchen in einem polymeren Bindemittel umfasst, wobei die porösen polymeren Teilchen folgende Formel haben:



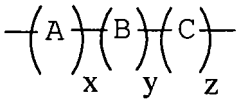
worin:

A Einheiten eines durch Additionspolymerisation polymerisierbaren Monomers darstellt, das mindestens zwei olefinisch ungesättigte Gruppen enthält;
B Einheiten von copolymerisierbaren Monomeren darstellt, die aus der aus Acrylmonomeren, Nitrilen und Amiden von Acrylsäure oder Methacrylsäure, Vinylverbindungen, aromatischen Verbindungen mit Vinylgruppen, Dialkylestem bestehenden Gruppe und Gemischen davon ausgewählt wurden;
C styrolische oder acrylische wiederkehrende Einheiten darstellt, die eine ionische Funktionalität aufweisen;
x zwischen etwa 27 und etwa 99 Mol-%;
y zwischen 0 und etwa 72 Mol-%; und
z zwischen etwa 1 und etwa 73 Mol-% liegt.

C) Beladen des Druckers mit einer Tintenstrahl-Tintenkomposition; und
D) Bedrucken der Bildempfangsschicht unter Verwendung der Tintenstrahl-Tintenkomposition entsprechend den digitalen Datensignalen.

Revendications

1. Elément d'enregistrement par jet d'encre comprenant un support revêtu d'une couche réceptrice d'image comprenant des particules polymères poreuses dans un liant polymère, les particules polymères poreuses ayant la formule :



dans laquelle :

A représente des motifs d'un monomère polymérisable par addition contenant au moins deux groupes ayant une insaturation de type éthylénique ;
B représente des motifs de monomères copolymérisables choisis dans le groupe comprenant des monomères acryliques, des nitriles et des amides d'acide acrylique ou d'acide méthacrylique, des composés vinyliques, des composés vinyliques aromatiques, des esters dialkyliques et des mélanges de ceux-ci ;
C représente des motifs récurrents styréniques ou acryliques contenant une fonction ionique ;
x est compris entre 27 et 99 % en moles ;
y est compris entre 0 et 72 % en moles ; et
z est compris entre 1 et 73 % en moles.

2. Elément selon la revendication 1, dans lequel ladite fonction ionique dudit motif récurrent styrénique ou acrylique est cationique.

3. Elément selon la revendication 2, dans lequel ladite fonction cationique est le chlorure de vinylbenzyltriméthylammonium, le chlorure de vinylbenzyl-N-butylimidazolium, le chlorure de vinylbenzyldiméthyldodécylammonium ou le chlorure de vinylbenzyldiméthyloctadécylammonium.

4. Elément selon la revendication 1, dans lequel ladite fonction ionique dudit motif récurrent styrénique ou acrylique est anionique.

5. Elément selon la revendication 4, dans lequel ladite fonction anionique est le sel de triméthylammonium de l'acide

méthacrylique, le sel de diméthylbenzylammonium de l'acide méthacrylique, le sel de diméthyldodécylammonium de l'acide méthacrylique ou le sel de méthyltrioctylammonium de l'acide styrènesulfonique.

6. Elément selon la revendication 1, dans lequel :

x est compris entre 55 et 99 % en moles ;
y est compris entre 0 et 44 % en moles ; et
z est compris entre 1 et 45 % en moles.

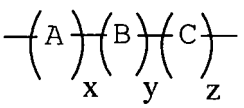
7. Elément selon la revendication 1, dans lequel lesdites particules polymères poreuses ont un diamètre moyen compris entre 0,05 et 10 μm.

8. Elément selon la revendication 1, dans lequel lesdites particules polymères poreuses ont un diamètre moyen compris entre 0,1 et 5 μm.

9. Elément selon la revendication 1, dans lequel ledit liant polymère comprend un alcool polyvinylique, une gélatine, un éther cellulosique, une poly(vinyl pyrrolidone) ou un poly(oxyde d'éthylène).

10. Procédé d'impression par jet d'encre comprenant les étapes de :

A) fourniture d'une imprimante à jet d'encre sensible aux signaux de données numériques ;
B) chargement dans ladite imprimante d'un élément d'enregistrement par jet d'encre comprenant un support revêtu d'une couche réceptrice d'image comprenant des particules polymères poreuses dans un liant polymère, les particules polymères poreuses ayant la formule :



dans laquelle :

A représente des motifs d'un monomère polymérisable par addition contenant au moins deux groupes ayant une insaturation de type éthylénique ;
B représente des motifs de monomères copolymérisables choisis dans le groupe comprenant des monomères acryliques, des nitriles et des amides d'acide acrylique ou d'acide méthacrylique, des composés vinyliques, des composés vinyliques aromatiques, des esters dialkyliques et des mélanges de ceux-ci ;
C représente des motifs récurrents styréniques ou acryliques contenant une fonction ionique ;
x est compris entre 27 et 99 % en moles ;
y est compris entre 0 et 72 % en moles ; et
z est compris entre 1 et 73 % en moles ;

C) chargement dans ladite imprimante d'une composition d'encre pour jet d'encre ; et
D) impression sur ladite couche réceptrice d'image en utilisant ladite composition d'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

- JP 7137433 A **[0008]**
- JP 11008569 A **[0009]**
- US 5840293 A **[0024] [0024]**
- US 5993805 A **[0024]**
- US 5403870 A **[0024]**
- US 5599889 A **[0024]**
- JP 5222108 A **[0024]**
- US 5288598 A **[0026]**
- US 5378577 A **[0026]**
- US 5563226 A **[0026]**
- US 5750378 A **[0026]**
- US 5279934 A **[0026]**
- US 4381946 A **[0033]**
- US 4239543 A **[0033]**
- US 4781758 A **[0033]**