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(54) Title: INK-JET RECORDING MEDIUM SYSTEM, METHOD FOR RECORDING AN IMAGE, AND THE RECORDED MEDIUM

(57) Abstract: An ink-jet or graphics arts recording media system comprising a support such as a canvas-like material with one or more coating layers, a novel ink-jet recording medium, a method for recording a water-resistant image on the medium using an ink-jet printer and the resulting recorded medium. The substrate of the recording media system provides high quality printed images when printed with an ink containing a reactive dye having ionizable and/or nucleophilic groups capable of reacting with the coating agent in one or more of the two layers. Images printed on this substrate are bleed-resistant, water- resistant (e.g., water-fast), and/or are characterized by an enhanced chroma and hue.

INK-JET RECORDING MEDIUM SYSTEM, METHOD FOR RECORDING AN IMAGE, AND THE RECORDED MEDIUM

Related Applications

The present application is a continuation of U.S. Serial No. filed March 7, 2006 which is a continuation of U.S. Provisional Application Serial No. 60/660,151, filed March 9, 2005.

Technical Field

The present invention relates generally to an ink-jet recording medium comprising a support such as a canvas-like material, and one or more coating layers thereon, and more particularly relates to a novel ink-jet recording medium, and a method for recording a water-resistant image on the medium using an ink-jet printer, and the resulting recorded medium, thereof.

Background

Ink jet printing technology is used for example for presentation (transparency), graphic arts, engineering drawing and home office applications. Digital graphics files are becoming increasingly popular and their resolution is also dramatically increasing. As the resolution and size of digital files increase, there is a need for media upon which such digital files can be reliably and durably printed that will provide realistic textures, such as photographic gloss, photographic matte finish and cloth or canvas-like textures. Another particular need is for a system and support for graphics arts printing wherein the support can yield a canvas-like appearance of the printed digital file.

The performance requirements for ink jet recording media used for these applications include efficient ink absorption, fast drying, good colorfastness, high image resolution, dimensional stability and archival stability of the printed image against the effects of light, atmospheric pollutants and humidity. As printing technology advances, paper manufacturers are faced with the increasingly rigorous demands of their customers for high quality paper that is economically attractive and provides a variety of textures.

For example, there is a great demand for paper of high enough quality to be suitable for printing of a digital image with an ink-jet printer where the look

and feel of the product approaches that of a photograph or a canvas painting. Thus, there is a keen demand for papers that meet high quality standards with respect to brightness, opacity, and dry and/or wet strength, and that, upon printing with any of a wide range of colorants, provide a water-resistant printed image. Customers further demand that such papers be amenable to use with a variety of printing techniques, including not only conventional printing techniques, but also "impact free" printing techniques such as inkjet printing (particularly colored inkjet printing), laser printing, photocopying, and the like.

Certain drawbacks and problems exist in the art that have stood in the way of a lot of customer satisfaction. For example, when an ink-jet receptive layer is coated upon a support there have been problems with peeling off of the coating, cracking of the coating, a lack of flexibility of the coating, bleeding of the ink, slow drying times that frequently lead to low satisfaction or poor quality results.

Although coating materials are effective to various degrees under certain conditions, use of each is associated with certain limitations. For example, it is often necessary to use large amounts of these conventional sizing agents in order to provide paper having the desired properties. However, the opacity and brightness of the paper substrate decrease in direct proportion to the amount of sizing agent applied to the paper. Moreover, as the amount of sizing agent and/or the cost of the sizing agent increases, the cost of producing the paper increases, making high quality papers prohibitively expensive. Certain sizing agents impart relatively poor bleed resistance and water resistance of imprinted inks, and thus must be used with insolubilizing agents to ensure production of a printed paper having satisfactory water resistance.

In addition, sizing agents usually require multiple application layers, which is time consuming and expensive. Also, beading of water from ink-jet inks can cause a specked or grainy image on the paper when the digital image sent to the printer was much clearer.

Conventional and modified starches are the most common sizing agents in use in the industry. Exemplary starch-based sizing agents include hydrophobic starches (see, e.g., U.S. Pat. No. 2,661,349), blends of hydrophobic and non-hydrophobic starches (see, e.g., U.S. Pat. No. 4,239,592; EP 350,668), and

blends of treated starches and/or cationic starches (see, e.g., U.S. Pat. No. 4,872,951; EP 620,315; U.S. Pat. No. 5,647,898). However, while starches may provide improved porosity, these compounds generally do not provide for improved bleed resistance or water resistance of inks printed on the treated paper substrates.

Several synthetic sizing agents are presently available, and may be used in internal sizing and/or external sizing processes. Exemplary synthetic sizing agents include hydrophobic cellulose reactive sizing agents (see, e.g., U.S. Pat. Nos. 4,478,682; 3,840,486), cationic polymers (see, e.g., U.S. Pat. No. 3,006,806), and water-soluble, poly(aminoamide) resins (see, e.g., U.S. Pat. No. 4,478,682). Synthetic compounds have also been used to enhance the dry and/or wet strength of paper (see, e.g., U.S. Pat. Nos. 5,138,669; 3,058,873; 5,510,004; 5,659,011), either at the internal sizing or external sizing steps. However, synthetic sizing agents tend to be expensive, due to both the cost of the starting material and the amount that is required to provide a paper substrate having the desired characteristics.

Use of conventional sizing agents normally results in a decrease in the porosity of the final substrate; thus, while the sized substrate may have the desired brightness and opacity, it may not provide for a printed image having a suitable optical density or color intensity. In addition, as the porosity of the paper increases, the paper becomes less amenable to various handling processes during manufacturing. For example, envelope manufacturers demand that the paper available to them have a relatively low porosity. If the porosity of the paper is too high, the paper is too stiff for handling by automated industrial devices for folding and sorting (e.g., devices of the "suction extractor" type) during envelope production. In contrast to lower porosity papers, high porosity papers also require slower machine speeds, and further require refining and draining operations that have relatively high energy costs. Both of these requirements result in decreases in plant productivity, efficiency, and cost effectiveness. Currently, there is no acceptable substrate, which is durable and provides a canvas-like texture and appearance upon recording of an image from an ink-jet printer.

There is a need in the field for coating agents and methods that provide an effective, cost efficient means for producing paper that yields a high quality, water-resistant printed image, that are amenable for use with a wide variety of paper substrates, and that are compatible with conventional manufacturing and post-manufacture handling processes. There is a need for agents that lend themselves to even a single coating layer, although multiple layers may be used. There is a particular need for coating agents and their coated substrate where an image printed using an ink-jet mechanism has the look and feel of a photograph or a canvas painting when produced by conventional photographic printing techniques.

Summary Of The Invention

It is a primary object of the invention to address the above-mentioned need in the art by providing a ink-jet recording medium that efficiently binds colorant upon printing, and thus provides an economical, efficient means for processing of a recording substrate to provide a high quality printed image thereon. A particular object of the invention is to provide a substrate having a high resolution digital image recorded thereon, wherein the recorded image has the appearance of a canvas-like painting.

Another object of the invention is to provide a printed, ink-jet recording medium on which the printed image is high quality (particularly with respect to optical density and brightness), bleed-resistant and water-resistant.

Still another object of the invention is to provide a method for recording an image or the ink-jet recording medium according to the present invention to provide water-resistant (e.g., water-fast) images thereon.

One embodiment of the present invention includes an ink jet recording media system that comprises a support and one or more coating layers thereon, wherein at least one coating layer comprises:

(a) a polyalkyloxazoline homopolymer at a weight percent from 5% to 35%,

(b) a member selected from a cross-linkable latex dispersion and ethylene-polyvinyl acetate at a weight percent from 10% to 75%, and

(c) a member selected from polymethyl acrylate trimethylammonium

chloride at a weight percent from 10% to 60% and polyhydroxyethylmethylmethacrylate-polyacrylic acid copolymer at a weight percent from 10% to 40%.

Another embodiment is constituted by one or more of the ink-jet media recording system coating layers described above may further comprise one or more of the following additional components:

(i) one or more member selected from polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, copolymers of hydroxymethylethacrylates and aminoacrylates and the corresponding salts of amino moiety of the copolymer, and terpolymers of hydroxyethylmethacrylates, aminoacrylates, acrylic acids and their amino salts at a weight percent from 10% to 35%

(ii) polyvinyl alcohols 10-35%

(iii) polyvinyl pyrrolidones 10-20%, and

(iv) an epichlorohydrin crosslinking compound, such as a polyamino amide epichlorohydrine adduct, at a weight percent from 1% to 5%.

A further embodiment of the present invention provides an inkjet recording medium suitable for recording images with dye and pigmented inks, comprising a support and one or more coating layers thereon, wherein at least one coating layer comprises:

(a) a polyalkyloxazoline homopolymer at a weight percent from 5% to 35%,

(b) a member selected from a cross-linkable latex dispersion and ethylene-polyvinyl acetate at a weight percent from 10% to 75%, and

(c) a member selected from polymethyl acrylate trimethylammonium chloride at a weight percent from 10% to 60% and polyhydroxyethylmethylmethacrylate-polyacrylic acid copolymer at a weight percent from 10% to 40%.

Yet a further embodiment the present invention provides a method for recording an image upon a substrate utilizing the ink-jet recording medium that is described above. Optionally, a commercial graphics art process can be utilized

to record the image by utilizing the coated substrate as described above.

The paper, cloth-like, canvas-like or metallic foil-like substrate provides high quality printed images when printed with an ink containing a reactive dye having ionizable and/or nucleophilic groups capable of reacting with the coating agent in one or more of the layers coated upon the substrate. Images printed on this substrate are bleed-resistant, water-resistant (e.g., water-fast), and/or are characterized by an enhanced chroma and hue. Such images sometimes take on the look and feel of a photograph or a canvas painting that is produced by conventional photographic or artistic processes.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

Detailed Description Of The Invention

Definitions and Nomenclature

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a monomeric" compound or "an oligomer" in a composition means that one or more different compounds or oligomers can be present in a homogenous composition or in a heterogeneous mixture.

The term "paper" or "paper substrate" with reference to the ink-jet recording medium is meant to encompass any substrate based on cellulosic fibers; synthetic polymer films and fibers such as polyamides, polyesters, polyethylene, and polyacrylic; inorganic fibers such as asbestos, ceramic, and glass fibers; and any combination of cellulosic, synthetic, and inorganic fibers or a combination of cellulosic fiber and synthetic polymer films produced by extrusion or coating the cellulosic fiber substrate. For another embodiment, the substrate comprising one or more coatings thereon may be a solid substrate, such as a flexible or rigid plastic substrate. In a particularly preferred embodiment, the substrate may be cloth-like, canvas like, or have a metallic foil appearance. The paper or paper substrate can be composed of compressed

natural or synthetic fibers, of compressed natural or synthetic solids, or of a woven appearance such as a textile or canvas. The paper or paper substrate may be an opaque or a see-through substrate such as used with an overhead projector, and the substrate may be of any dimension (e.g., size or thickness) or form (e.g., pulp, wet paper, dry paper, etc.). As noted above, the paper or paper substrate can have a smooth or textured appearance, e.g., a canvas-look texture, or perhaps a metallic foil-like appearance. In most instances, the "paper" or "paper substrate" has been subjected to an external sizing process prior to treatment according to the methods of the invention, however sizing is not required. The paper substrate is preferably in the form of a flat or sheet structure, which structure may be of variable dimensions (e.g., size and thickness). "Paper" is meant to encompass printing paper (e.g., inkjet printing paper, etc.), writing paper, drawing paper, and the like, as well as board materials such as cardboard, poster board, Bristol board, flexible and inflexible canvas, flexible cloth, cloth or canvas laminated to a hard or flexible support, and the like.

The term "sheet" or "flat structure" is not meant to be limiting as to dimension, roughness, or configuration of the substrate useful with the present invention, but rather is meant to refer to a product suitable for coating. A sheet or flat structure can refer to a substrate having either a substantially smooth or a textured appearance, e.g., a canvas-look texture.

"Sized paper substrate" is a paper substrate as described above that has applied to its surface and/or is saturated with a sizing composition. Sizing compositions may be applied in an internal sizing step and/or in an external sizing step; preferably sizing (e.g., internal and/or external sizing) occurs prior to application of the coating composition of the invention.

"Coated paper substrate" is a paper substrate that has applied to its surface and/or is saturated with a coating composition of the invention. Coating compositions may be applied as a pre-treatment (e.g., prior to printing), simultaneously with printing, or as an after-treatment. The coating compositions of the invention are applied in quantities suitable to provide the desired characteristics, such as bleed resistance, water resistance (e.g., water-fastness) of an ink printed on coated paper substrate, etc. Multiple coatings may be

applied, but one embodiment consists of a single application of the coating composition on one or both sides of a substrate to produce a high quality coated paper substrate.

"Aqueous based ink" refers to an ink composed of an aqueous carrier medium (or composed of a mixed solvent medium such as a mixture of aqueous and aqueous miscible organic solvents) and a colorant, such as a dye or a pigment dispersion. An "aqueous carrier medium" is composed of water or a mixture of water and one or more water-soluble organic solvents. Exemplary aqueous based ink compositions are described in detail below.

"Colorant" as used herein is meant to encompass one or more organic dyes, inorganic dyes, pigments, stains, and the like compatible for use with the polymer coatings of the invention.

A colorant may be in the RGB scale, the CMY scale, or simply a white or black opaque pigment. Examples of opaque pigments are aluminas, silicas, and titanium oxide. Examples of organic pigments are micronized organic polymers that are usually not soluble in water.

The term "organic solvent" is used herein in its conventional sense to refer to a liquid organic compound, typically a monomeric organic material in the form of a liquid, preferably a relatively non-viscous liquid, the molecular structure of which contains hydrogen atoms, carbon atoms, and optionally other atoms as well, and which is capable of dissolving solids gases or liquids.

The terms "significant" or "significantly", as when used with reference to "significantly enhanced brightness" or "significantly improved water-fastness" generally refer to a difference in a quantifiable, measurable, or otherwise detectable parameter, e.g., optical density, LAB graphs (color sphere), dot spread, bleed through, between the two groups being compared (e.g., uncoated versus coated paper substrates) that is statistically significant using standard statistical tests. For example, the degree of visual wicking or water-fastness in a coated paper substrate as detected in a print assay may be quantified using standard methods, and the degree of wicking or water-fastness under different conditions can be compared for both coated and uncoated paper substrates to detect statistically significant differences.

Photograph-like quality "look and feel", when used herein refers to a printed substrate wherein the image is substantially free of the type of speckling or graininess that is usually caused by uneven absorption (or by incomplete absorption) of water soluble inks into the substrate after printing and before drying, and may be glossy, dull or semi-glossy, oily, metallic, or oil painting-like in appearance based upon the desired result and the desired coating composition.

The term "fluid resistance" is used herein to describe the resistance of a paper substrate to penetration by a fluid, with the term "water resistance" specifically referring to resistance of a paper substrate to penetration by a fluid.

The term "water-fast," is used herein to describe a form of water resistance, and which is normally used to refer to the nature of the ink composition after drying on a substrate. In general, "water-fast" means that the dried composition is substantially insoluble in water, such that upon contact with water, the dried ink retains at least about 70%, preferably at least about 85%, and more preferably at least about 95%, of optical density.

The term "bleed resistance" is meant to refer to the retardation of the penetration of water into paper, which retardation is associated with creation of a low energy hydrophobic surface at the fiber-water interface which increases the contact angle formed between a drop of liquid and the surface, and thus decreases the wettability. Contact angles have been shown to be sensitive to molecular packing, surface morphology, and chemical constitution of the paper substrate and any components added thereto.

The term "rub resistance" is normally meant to refer to a characteristic of the ink composition after drying on a substrate, more specifically, the ability of a printed image to remain associated with the substrate upon which it is printed despite application of force (e.g., rubbing) to the printed image. In general, "rub resistant" means that the dried ink composition is substantially resistant to rubbing force so that the dried ink retains at least about 70%, preferably at least about 85%, and more preferably at least about 95%, of optical density after rubbing of the printed image.

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n-

propyl, isopropyl, n-butyl, isobutyl, t-butyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. The term "lower alkyl" intends an alkyl group of 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms.

The term "alkylene" as used herein refers to a difunctional, branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, including without limitation methylene, ethylene, ethane-1,1-diyl, propane-2,2-diyl, propane-1,3-diyl, butane-1,3-diyl, and the like. "Lower alkylene" refers to an alkylene group of 1 to 6 carbon atoms.

The term "alkoxy" as used herein intends an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be defined as --OR where R is alkyl as defined above. A "lower alkoxy" group intends an alkoxy group containing 1 to 6 carbon atoms.

"Halo" or "halogen" refers to fluoro, chloro, bromo or iodo, and usually relates to halo substitution for a hydrogen atom in an organic compound.

The term "polymer" is used herein in its conventional sense to refer to a compound having about 8 or more monomer units, and unless otherwise stated, refers to a compound having a molecular weight from about 1000 and higher. The term "oligomer" refers to a compound having from 2 to about 8 monomer units. The terms oligomer and polymer intend to cover compounds having a single type of repeating monomer unit (homopolymer or oligomer) as well as compounds containing more than one type of monomer unit (copolymers and mixed oligomers). The terms "monomer" or "monomeric" as used herein refer to compounds which are not polymeric or oligomeric as defined above.

Optionally" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not. For example, the phrase "optionally substituted" aromatic ring means that the aromatic ring may or may not be substituted and that the description includes both an unsubstituted aromatic ring and an aromatic ring bearing one or more substituents.

Overview of the Invention

The present invention is based upon the discovery of advantages provided by an ink-jet or graphics arts recording system media comprising a support and one or more coating layers thereon, wherein at least one coating layer comprises:

(a) a polyalkyloxazoline homopolymer at a weight percent from 5% to 35%,

(b) a member selected from a cross-linkable latex dispersion and ethylene-polyvinyl acetate at a weight percent from 10% to 75%, and

(c) a member selected from polymethyl acrylate trimethylammonium chloride at a weight percent from 10% to 60% and polyhydroxyethylmethylmethacrylate-polyacrylic acid copolymer at a weight percent from 10% to 40%.

One or more of the ink-jet media recording system coating layers described above may further comprise one or more of the following additional components:

(i) one or more member selected from polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, copolymers of hydroxymethylethacrylates and aminoacrylates and the corresponding salts of amino moiety of the copolymer, and terpolymers of hydroxyethylmethacrylates, aminoacrylates, acrylic acids and their amino salts at a weight percent from 10% to 35%

(ii) polyvinyl alcohols 10-35%

(iii) polyvinyl pyrrolidones 10-20%, and

(iv) an epichlorohydrin crosslinking compound, such as a polyamino amide epichlorohydrine adduct, at a weight percent from 1% to 5%.

The present invention provides an inkjet recording medium suitable for recording images with dye and pigmented inks, comprising a support and one or more coating layers thereon, wherein at least one coating layer comprises:

(a) a polyalkyloxazoline homopolymer at a weight percent from 5% to 35%,

(b) a member selected from a cross-linkable latex dispersion and ethylene-polyvinyl acetate at a weight percent from 10% to 75%, and

(c) a member selected from polymethyl acrylate trimethylammonium chloride at a weight percent from 10% to 60% and polyhydroxyethylmethylmethacrylate-polyacrylic acid copolymer at a weight percent from 10% to 40%.

Further, the present invention provides a method for recording an image upon a substrate utilizing the ink-jet recording medium that is described above. Optionally, a commercial graphics art process can be utilized to record the image by utilizing the coated substrate as described above.

In a preferred embodiment, the recording media system as described above optionally further contains one or more of pigment dispersions, surfactants and other additives at a weight percent from 10% to 45%. One or more of the coating layers may optionally comprise one or more pigments, fillers or organic particulates selected from the group consisting of amorphous silica, crystalline silica, aluminum trihydrate, kaolin, talcum, chalk, betonite, zeolite, glass beads, calcium carbonate, potassium sodium aluminum silicate, diatomaceous earth, silicates of aluminum, silicates of magnesium, titanium doxide, polyolefins, polystyrene, polyurethane, starch, poly(methyl methacrylate) and polytetrafluoroethylene.

In a preferred embodiment, the recording media system described above comprises a pigment dispersion at a weight percent from 15% to 45%. Particularly preferred pigment dispersions are a silica pigment dispersion, an alumina pigment dispersion, or a mixture thereof.

In one embodiment of the recording media system described above, one or more of the coating layers comprises an ink jet receptive layer.

In a further embodiment, the recording media system of the invention further comprises a barrier layer between the support and the ink receptive layer or layers.

With respect to such a media system having an image recorded thereon, the recording media system described above is one wherein one or more of the coating layers further comprise ink jet ink.

To optimize the characteristics of the recording media, the recording media may further comprise one or more additives selected from the group consisting of surface active agents, antistatic agents, thickeners, suspending agents, pH controlling compounds, light stabilizers, antioxidants, humectants, bacteriostats, cross-linking agents and optical brighteners, and flavoring agents.

For enhanced longevity and appearance, the recording media system described above may include one or more additives selected from the group consisting of phenolic antioxidants, hydroxybenzotriazole ultraviolet light absorbers, benzophenone ultraviolet light absorbers, hydroxyphenyltriazine ultraviolet light absorbers and hindered amine light stabilizers.

In a preferred embodiment, the recording media system described above includes a support comprising cellulose, cellulose esters, cellulose acetate, polyesters, polystyrene, polyethylene, poly(vinyl acetate), polypropylene, polycarbonate, polymethacrylic acid and methyl and ethyl esters, polyamides such as nylons, polyesters such as poly(ethylene terephthalate) (PET), polyimides, polyethers, polyvinyl chloride polytetrafluoroethylene, polyvinylidene fluoride or polysulfonamides. Such a support may be a paper or transparent poly(ethylene) terephthalate or a metallic foil. A preferred support is a fabric or fabric-like support, such as a cloth, canvas, or other similar flexible support.

The invention provides a method for preparing an ink jet recording media system, which method comprises applying one or more coating layers on a support to provide one or more coating layers as described above, wherein at least one of the coating layers is a coating layer according to the media system described above.

The invention also provides a substrate support for ink jet or graphics arts recording of a digital image comprising the ink jet recording media system described above. A preferred substrate support for ink jet recording is one wherein the substrate support comprises cellulose, cellulose esters, cellulose acetate, polyesters, polystyrene, polyethylene, poly(vinyl acetate), polypropylene, polycarbonate, polymethacrylic acid and methyl and ethyl esters,

polyamides such as nylons, polyesters such as poly(ethylene terephthalate) (PET), polyimides, polyethers, polyvinyl chloride polytetrafluoroethylene, polyvinylidene fluoride or polysulfonamides. Also, the substrate support for ink jet recording may be a support that is paper or transparent poly(ethylene) terephthalate, or the support may be a metal deposited foil substrate of various colors. A preferred support recording media system is a fabric-like support, such as a cloth, canvas, or other similar flexible support that provides a recorded image with an oil or water-color painting type of appearance.

The ink-jet recording media system according to the invention yields high quality printed images having improved color fastness (the printed images do not run when exposed to moisture) as a result of the substantially non-reversible binding of aqueous colorants to the coating agent present in layer so coating composition(s) on the ink-jet recording medium. These images are therefore characterized as "water-resistant" or "water-fast" due to the characteristics of the printed image following exposure to water. Often the printed images are substantially similar to the look and feel of a photographic image or of a canvas painting.

The coated paper substrates (ink-jet recording medium) of the invention can be used in conventional printing, or with digital printing (particularly inkjet printing, including drop-on-demand printing and continuous printing) to provide highly brilliant, printed images that are significantly improved in color quality (for example, with respect to chroma and hue) when compared to uncoated paper substrates and/or to paper substrates coated with conventional coating compositions. The coating compositions and their methods of use according to the present invention thus provide a number of advantages over conventional sizing and coating methods, and sizing and coating compositions.

The coating layers of the invention can be readily prepared from commercially available starting materials and/or reagents, are compatible with additional binders or additives, can be used with a variety of base papers, and are compatible with a variety of printing methods, including conventional and digital printing methods (particularly inkjet printing, including drop-on-demand printing and continuous printing), and can also be used with existing commercial paper production processes and equipment. The coating composition for each of

the layers of the ink-jet recording medium are inexpensive to prepare, and relatively small amounts are required to provide an ink-jet recording medium having the advantageous features described herein. The coating compositions used for each of the layers of the ink-jet recording medium of the invention are also easy to handle due to their solubility in water (the active components, the coating agents, are hydrophilic polymers), and do not require the use of large volumes of organic solvents. Such coating compositions also possess good film-forming properties.

The ink-jet recording medium is a coated paper substrate prepared as described herein which exhibits improved durability, as evidenced by improved paper strength (e.g., tear strength), and stability upon prolonged storage. The ink-jet recording medium does not discolor or yellow, and maintains a high degree of brightness for extended periods of time. Paper substrate ink-jet recording mediums according to the invention react rapidly and, in some embodiments, irreversibly with a number of aqueous based colorants, thus providing a versatile coating system for use with a wide variety of available colorants. Furthermore, because the colorant reacts quickly with the layers of coating compositions, the recorded ink-jet recording medium does not require a separate curing step, but rather is fast-drying. This fast-drying characteristic provides for printed images that are "non-sticky," thus allowing the ink-jet recording medium to be handled immediately after printing, e.g., to allowing stacking. The ink-jet recording medium of the invention can also be used to prepare images with varying degrees of gloss, depending upon variations in pigment.

In addition to their water resistance, ink-jet recording medium paper substrates according to the invention are highly bleed-resistant (as evidenced by small dot size measurements, i.e., less wicking action) and rub-resistant.

A preferred ink-jet recording media system according to the invention is wherein one or more of the coating layers comprise polymers that are soluble in an aqueous solvent or are soluble in an solvent mixture of an aqueous solvent and a polar organic solvent. A particularly preferred polar organic solvent is an alcohol.

A preferred such ink-jet recording medium as described above is wherein at least one layer contains an ammonium salt of at least one polymer that is soluble in an aqueous solvent or in a solvent mixture of an aqueous solvent and a polar organic solvent and the polymer is a member selected from a group hydroxyethylmethacrylate copolymer or terpolymer, or a derivative thereof, wherein the copolymer or terpolymer comprises at least one member of the group consisting of 2-hydroxyethylmethacrylate/co-acrylic acid copolymer, 2-hydroxyethylmethacrylate/methacrylic acid copolymer, 2-hydroxyethyl-methacrylate/dimethylaminopropylmethacrylate, 2-hydroxyethylmethacrylate/dimethyl-aminoethylmethacrylate, and 2-hydroxyethylmethacrylate-vinylpyrrolidone, quaternized polyhydroxyethlymethacrylate-co-dimethylaminopropylmethacrylate, quaternized polyhydroxyethlymethacrylate-co- dimethylaminoethylmethacrylate; Vinylpyrrolidone polymers and copolymers are selected from the group consisting polyvinylpyrrolidone vinylpyrrolidone/dimethylaminoethyl methacrylate copolymer, vinyl caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylate terpolymer, vinylcaprolactam/vinylpyrroldone/dimethylaminopropyl methacrylamide terpolymer, vinylpyrrolidone/dimethylaminopropyl methacrylamide copolymer, vinylpyrrolidone/dimethylaminoethyl methacrylate copolymer, and quaternized derivatives thereof.

In one embodiment of such an ink-jet recording media system, at least one of the layers contains at least one cross-linker selected from group of polyamide-epichlorhydrin resin and polyfunctional aziridine or mixture thereof. One of the layers may also comprise a plasticizer which is a member selected from the group consisting of phosphates, substituted phthalic anhydrides, glycerols, and polyglycols. A preferred plasticizer is polyvinyl alcohol, polyethylene glycol or a derivatives thereof.

In another embodiment according to the invention the second layer of the ink-jet recording medium further comprises a white pigment.

The coating layers can further comprise organic particulates selected from the group consisting of starch, polyolefins, poly(methyl methacrylates), polystyrenes, polytetrafluoroethylenes, and polyurethanes. Also, the second

layer can further comprise additives selected from the group consisting of antifoam agents, surfactants, dyestuffs, optical brighteners, and mixtures thereof.

A preferred ink-jet recording medium of the invention is wherein the substrate is a paper or polymeric film. A preferred substrate is a paper selected from the group consisting of plain, clay-coated, resin-coated, and latex-saturated papers. Another preferred substrate is a polymeric film selected from the group consisting of polyvinyl chloride, polyethylene, polypropylene, polycarbonate, polyimide, polyester, and fluoroplastic films. A further preferred substrate is a cloth-like or canvas-like substrate that may comprise one or more of comprises cellulose, cellulose esters, cellulose acetate, polyesters, polystyrene, polyethylene, poly(vinyl acetate), polypropylene, polycarbonate, polymethacrylic acid and methyl and ethylesters, polyamides such as nylons, polyesters such as poly(ethylene terephthalate) (PET), polyimides, polyethers, polyvinyl chloride polytetrafluoroethylene, polyvinylidene fluoride or polysulfonamides.

In one preferred embodiment, the inkjet recording medium comprises a coated substrate that is glossy and opaque, transparent, translucent, matte, or non-glossy opaque. Another preferred such medium is a coated substrate that provides an oil or water-color ready canvas or cloth.

The inkjet recording medium of the present invention may comprise a substrate wherein one or more functional or non-functional coating layers are placed between the paper substrate and the one or more coating layers, such as a barrier layer as described in published U.S. Patent application 20050019507, published January 27, 2005.

In one embodiment the present invention provides a method for providing a water-resistant image on the ink-jet recording medium of the invention as described above, comprising applying an ink composition to the recording medium, wherein the ink composition comprises a dye having ionizable and/or nucleophilic groups capable of reacting with a dye-fixing compound. A preferred such method is wherein the dye composition is a predominantly aqueous based ink or is an ink having a mixed solvent of at least one aqueous solvent and at least one aqueous miscible organic solvent.

In one embodiment, the invention provides a printed paper product, printed canvas product, or printed cloth product prepared by the method

described above. A preferred printed paper product prepared by the above method is wherein one surface of the paper has an adhesive backing that is optionally removable. A preferred canvas or cloth product has an adhesive backing that is optionally removable to provide adhering of the substrate that has the recorded image to an inflexible or flexible support.

Commercially available such polymers include "AMRES.RTM.," available from Georgia Pacific, Resins, Inc., Atlanta, Ga., "KYMENE.RTM.," from Hercules, Inc., Wilmington, Del., and "Polycup.RTM.," also from Hercules, Inc. These azetidinium polymers are generally referred to as poly(aminoamide)-epichlorohydrin (PAE) resins; such resins are typically prepared by alkylating a water-soluble polyamide containing secondary amino groups with epichlorohydrin. Other suitable azetidinium polymers will be known to those skilled in the art and/or are described in the pertinent texts, patent documents, and literature references; see, for example, Moyer, et al., in Wet Strength in Paper and PaperBoard, Tappi Monograph Series No. 29, Tappi Press, Ch. 3, p. 33-37 (1965); Chan, in Tappi Wet and Dry Strength Short Course, Tappi Press, Atlanta, Apr. 13-15, 1988; and Espy, in Wet Strength Resins and Their Application, Ed., Lock L. Chan, Tappi Press, Atlanta, Ga. (1994).

An examples of other such compounds is are polyvinylamidine (PVAD). Esprit Chemicals, www.espritchem.com (Tele. 941-355-5100, 1-800-237-7748, fax 941-358-1339) provides a vinylamide type polymer PVAM-0595B, a homopolymer of vinyl amine. Preferred compounds are the alkanoyl salts of these polymers such as gluconate or gluconate derivative salts. The PVAM polymers tend to form amides when reacted with acids and may be utilized in the present invention.

In one embodiment the polymeric binder is a film-forming binder selected from the group consisting of polysaccharides, polypeptides, synthetic vinyl polymers, cationic film-forming binders, and derivatives thereof. Preferred polysaccharide binders are selected from the group consisting of starch, a cellulosic polymer, dextran and the like. Preferred polypeptide binders are selected from the group consisting of collagen and gelatin. Preferred synthetic film-forming binders are a member selected from the group consisting of a synthetic vinyl polymer or polyethyloxazoline monomer units. Preferred synthetic

vinyl polymers are selected from the group consisting of poly(vinyl alcohol), poly(vinyl phosphate), poly(vinyl pyrrolidone), vinyl-pyrrolidone-vinyl acetate copolymers, vinyl acetate-acrylic acid copolymers, vinyl alcohol-vinyl acetate copolymers, vinyl pyrrolidone-styrene copolymers, poly(vinylamine) and polyethyloxazoline, or a quaternary salt thereof. A more preferred synthetic vinyl polymer binder is a vinyl pyrrolidone-styrene copolymer or quaternary salts thereof.

Preferred film forming binders comprise at least one cationic film-forming binder. More preferred cationic film-forming binders are quaternized members selected from the group consisting of a vinyl pyrrolidone-dimethylaminoethylmethacrylate copolymer, dimethyl-aminoethylmethacrylate-co-methyl methacrylate, 2-hydroxyethyl methacrylate-dimethyl-aminoethylmethacrylate, 2-hydroxypropylmethacrylate-dimethyl aminoethylmethacrylate, polydiallyldimethyl ammonium chloride and quaternized aminoacrylate polymers. Even more preferred is the cationic film-forming binder which is a salt having as the anion counter-ion a member selected from the group consisting of halide, hydrogen sulfate, acetate, methane sulfonate, succinate, citrate, malonate, fumarate, oxylate, gluconate or a gluconate derivative. Most preferred is where such cationic film-forming binder salts have the anion of the salt as gluconate or a gluconate derivative.

In one embodiment the coating composition according to the invention further includes a colorant or pigment, particularly silicas, aluminas, titanium dioxide, and the like. The colorant or pigment can be a white or black opaque pigment.

In a preferred embodiment of the invention, one of the coating layers comprises an ink receptive coating composition or agent represents approximately 5 wt. % to 55 wt. % of the coating composition, based upon total solids weight of the composition after drying.

In one embodiment the present invention provides an ink-jet recording medium which is an optionally pre-sized paper product coated by coating composition as described above wherein the ink receptive surface coating agent or composition comprises a member selected from the group consisting of

chlorhexidine or a salt thereof, chlorguanide or a salt thereof, polyvinyl amidine (PVAD) or a salt thereof, or mixtures of two or more of these.

The coating agents are as described above. In some embodiments of the invention, it is important that the pH of the coating composition be acidic, as some compositions can tend to gel at basic pH. In such cases, if necessary, an acid should be added to the composition to ensure that the pH is below 7.0, preferably less than about 6.5, and most preferably in the range of about 1.0 to 6.5. Suitable acids include sulfuric acid, hydrochloric acid, acetic acid, and the like.

The coating compositions in the layers of the invention recording medium preferably include a film-forming binder. By "film-forming binder" is meant a substance that provides for improved strength of a paper substrate upon application of the substance to the substrate. "Film-forming binders" used in connection with the coating compositions of the invention include any film-forming binder that is compatible with the selected coating agent and other components of the coating composition. Exemplary film-forming binders include, but are not necessarily limited to: polysaccharides and derivatives thereof, e.g., starches, cellulosic polymers, dextran and the like; polypeptides (e.g., collagen and gelatin); and synthetic polymers, particularly synthetic vinyl polymers such as poly(vinyl alcohol), poly(vinyl phosphate), poly(vinyl pyrrolidone), vinyl-pyrrolidone-vinyl acetate copolymers, vinyl alcohol-vinyl acetate copolymers, vinyl pyrrolidone-styrene copolymers, and poly(vinyl amine), and cationic film-forming binders such as quaternized vinyl pyrrolidone-dimethylaminoethyl-methacrylate copolymer, dimethylaminoethyl-methacrylate-co-methyl methacrylate, polydiallyl dimethyl ammonium chloride and quaternized aminoacrylate polymers.

Polysaccharide binders: Starches, as noted above, represent one category of suitable film-forming binders for use herein. Suitable starches may be any of a variety of natural, converted, and synthetically modified starches. Exemplary starches include, but are not necessarily limited to starch (e.g., SLS-280 (St. Lawrence Starch)), cationic starches (e.g., Cato-72 (National Starch), hydroxyalkylstarch, wherein the alkyl has at least one carbon atom and wherein the number of carbon atoms is such that the material is water soluble, preferably

from about 1 to about 10 carbon atoms, such as methyl, ethyl, propyl, butyl, or the like (e.g, hydroxypropyl starch #02382 (PolySciences, Inc.), hydroxyethyl starch #06733 (PolySciences, Inc.), Penford Gum 270 and 280 (Penford), and Film-Kote (National Starch)), starch blends (see, e.g., U.S. Pat. No. 4,872,951, describing a blend of cationic starch and starch treated with an alkyl or alkenyl succinic anhydride (ASA), preferably 1-octenyl succinic anhydride (OSA)), and the like. The film-forming binder can also be a synthetically produced polysaccharide, such as a cationic polysaccharide esterified by a dicarboxylic acid anhydride (see, e.g., U.S. Pat. No. 5,647,898). Additional saccharide binders include cellulosic materials such as alkyl celluloses, aryl celluloses, hydroxy alkyl celluloses, alkyl hydroxy alkyl celluloses, hydroxy alkyl celluloses, dihydroxyalkyl cellulose, dihydroxyalkyl cellulose, hydroxy alkyl hydroxy alkyl cellulose, halodeoxycellulose, amino deoxycellulose, dialkylammonium halide hydroxy alkyl cellulose, hydroxyalkyl trialkyl ammonium halide hydroxyalkyl cellulose, dialkyl amino alkyl cellulose, carboxy alkyl cellulose salts, cellulose sulfate salts, carboxyalkylhydroxyalkyl cellulose and the like). Still additional film-forming binders of this type include dextran (e.g., dialkyl aminoalkyl dextran, amino dextran, and the like), carrageenan, Karaya gum, xanthan, guar and guar derivatives, (e.g., carboxyalkyl hydroxyalkyl guar, cationic guar, and the like), and gelatin.

Additional exemplary film-forming binders include resins (e.g., such as formaldehyde resins such as melamine-formaldehyde resin, urea-formaldehyde resin, alkylated urea-formaldehyde resin, and the like), acrylamide-containing polymers (e.g., poly(acrylamide), poly(N,N-dimethyl acrylamide), and the like), poly(alkyleneimine)-containing polymers (e.g., poly(ethyleneimine), poly(ethyleneimine)epichlorohydrin, alkoxylated poly(ethyleneimine), and the like), polyoxyalkylene polymers (e.g, poly(oxymethylene), poly(oxyethylene), ethylene oxide/propylene oxide copolymers, ethylene oxide/2-hydroxyethyl methacrylate/ethylene oxide and ethylene oxide/hydroxypropyl methacrylate/ethyleneoxide triblock copolymers, ethylene oxide-4-vinyl pyridine/ethylene oxide triblock copolymers, ethylene oxide-isoprene/ethylene oxide triblock copolymers, epichlorohydrin-ethylene oxide copolymer, and the

like), etc. Other examples are film forming binders comprising 2-hydroxyethylmethacrylate copolymer or terpolymer, or a derivative thereof.

Examples of 2-hydroxyethylmethacrylate copolymer or terpolymer, or a derivative thereof, are wherein the copolymer or terpolymer is at least one member of the group consisting of 2-hydroxyethylmethacrylate/co-acrylic acid copolymer, 2-hydroxyethylmethacrylate/meth-acrylic acid copolymer, 2-hydroxyethyl-methacrylate/dimethylaminopropylmethacrylate, 2-hydroxyethylmethacrylate/dimethyl-aminoethylmethacrylate, and 2-hydroxyethy-lmethacrylate-vinylpyrrolidone, and the like.

Such film forming binders can further comprise at least one additional film forming binder selected from the group consisting of (a) polyvinyl alcohol or a copolymers comprising vinyl alcohol monomer units, (b) polyvinylpyrrolidone or a copolymer comprising vinylpyrrolidone monomer units, (c) cellulose or a cellulose derivative, (d) starch or a starch derivative, (e) a vinyl acetate polymer or a copolymer comprising vinyl acetate monomer units, and (f) polyethyloxazolidine, or a quaternized derivative thereof.

Any of the above exemplary film-forming binders can be used in any effective relative amounts, although typically the film-forming binder, if present in the proportions as described above in the description of the coating composition proportions. Starches and latexes are of particular interest because of their availability and applicability to paper.

Additional coating composition components in each of the two layers for the ink-jet recording medium according to the invention may include, but are not necessarily limited to, inorganic fillers, anti-curl agents, or additional conventional components such as a surfactant, plasticizer, humectant, UV absorber, light fastness enhancer, polymeric dispersant, dye mordant, optical brightener, or leveling agent, as are commonly known in the art. Illustrative examples of such additives are provided in U.S. Pat. Nos. 5,279,885 and 5,537,137. Of particular interest is the inclusion of additional components that provide for a coated substrate having a non-glossy, matte, or glossy surface; as will be appreciated by those skilled in the art, incorporation of a pigment (e.g., silica, calcium carbonate) will generally give rise to a non-glossy surface, while a glossy surface will result in the absence of a pigment (or in the presence of only a small amount

of pigment), provided that the underlying substrate surface has a glossy finish at the outset (e.g., is resin coated or the like).

Examples of coating composition are compositions as described above, wherein:

In one preferred embodiment, the coating compositions for each of the layers as described above are coating compositions in an aqueous solvent or in a mixed solvent of at least one aqueous solvent and at least one aqueous miscible organic solvent.

The coating compositions for each of the two layers may also contain a colorant, e.g., a pigment, dye or other colorant, to provide for whiteness or color of the coated paper substrate. The coating compositions may also further include a cross-linking agent, such as zirconium acetate, ammonium zirconium carbonate, or the like, for intra-molecular and/or intermolecular cross-linking of coating agents in the coating composition, and/or a chelating agent such as boric acid. Additional components that may be desirable for use in the coating compositions of the invention, as well as guidance for the use of such components and a general description of paper chemistry, are found in Paper Chemistry, 2nd Edition, Roberts, ed., Blackie Academic & Professional, Glasgow, UK (1994). For example, surfactants, leveling agents, and de-foaming agents may also be utilized in the coating compositions.

The coating compositions for each of layers (a) and (b) are preferably provided in an aqueous liquid vehicle, that only contains small amounts of a water-soluble organic solvent may be present. However, the aqueous liquid vehicle (generally water) may contain other non-organic compounds which are water soluble (smaller amounts) or water miscible. It may on occasion be necessary to add a solubilizing compound during preparation of the coating composition so that the components dissolve in the aqueous liquid vehicle, e.g., an inorganic base such as ammonia and/or an organic amine. Suitable organic amines include lower alkyl-substituted amines such as methylamine, dimethylamine, ethylamine, and trimethylamine, as well as ethanolamine, diethanolamine, triethanolamine, and substituted ethanolamines, typically lower alkyl-substituted ethanolamines such as N-methyl and N,N-dimethyl ethanolamines, and morpholine. Such compounds are also useful for bringing

the pH into the desired range for basic formulations, and, if present, will generally represent not more than about 20 wt. % of the composition, and in most cases will represent not more than about 10 wt. % of the composition.

Application of Coating Compositions to Paper Substrates

The coating compositions for each coating layer on the ink-jet recording medium according to the invention can be applied to a substrate, e.g., a paper substrate, by any of a number of conventional processes commonly employed in the art. The substrate as defined above can be make of natural or synthetic fibers or of simply pressed or molded solids, in addition sheets of substrate can be woven such as in fabric or canvas, and can optionally be a coated substrate prior to use of the present coating composition. In essence, the base stock or fibrous cellulosic substrate to be coated in accordance with the present invention can be one of a wide variety of types depending upon the intended use of the final product. The paper substrate is optionally pre-sized, either internally or externally, and can vary in weight from lightweight papers to the heavier paperboards. However, where the coating is applied on-machine, in order to achieve acceptable manufacture speeds (e.g., 100 to 3000 ft./per minute), it is recommended that the weight of the paper base be greater than 30 grams per square meter. When the final product is to exhibit gloss at a satisfactory level (generally greater than 50), the base sheet, before it receives the top coating, should retard rapid drainage of the water or of the coating into the substrate. One way to accomplish this is by sizing the sheet, either internally or externally but generally externally. Preferably, external sizing is included in an intermediate impregnation coating which serves as a base for the top coating. The paper substrate can be texturized before or after coating to give different surface grains (e.g., such as molding or stamping a texture on the substrate).

Each of the coating composition layers can range in thickness from several hundred Angstroms to several mils in thickness, e.g., in the range of approximately 100 Angstroms to 5 mm; typical amounts of the coating composition to be applied generally range from about 50 to about 500 pounds per ton of substrate, or about 2 to 30 g/m.sup.2. In one embodiment, the coating composition is applied so that the first layer does not substantially infiltrate into

the substrate (e.g., the substrate is of a porosity such that the coating composition does not substantially penetrate beyond or far beyond the substrate surface). Application of a coating in a selected thickness can readily be done by one of skill in the art using known techniques, for example, by varying the coating agent concentration and number of coatings and through selection of the application means.

The coating compositions layers as described above are applied to any desirable paper substrate, usually to a type of pre-sized paper substrate commonly used in printing. Substrates for use in the invention include cellulose and non-cellulose type substrates (e.g., synthetic fibers such as polyamides, polyesters, polyethylene, and polyacrylic fibers; inorganic fibers such as asbestos, ceramic, and glass fibers), and/or any combination of cellulosic, synthetic, and inorganic fibers, with porous cellulose substrates being preferred. A preferred substrate for use herein is generally free cut sheet paper, with exemplary paper substrates including, but not limited to, copier grade paper, business card stock, resin-coated papers, cartons such as milk cartons and cardboard gift boxes. Additional exemplary substrates for use in the invention include polyester films such as "MYLAR" flexible film, polysulfones, polyvinyls, cellulose triacetates, and the like. Coated transparent films are also contemplated. Woven fabrics or simulated woven fabrics may also be used as the substrate. Molded sheets can be utilized. Further the paper substrate can have one or more adhesive layers which are optionally removable, before or after printing.

Processes for coating pre-sized paper substrates are well known in the art, and can be performed either on-machine, as alluded to above, or off-machine, i.e., subsequent to completion of paper manufacture. Generally, coating is accomplished by dip coating, reverse roll coating, extrusion coating, saturation, and the like.

Method for Providing Water-Resistant Images on Coated Paper

The invention also features a method for providing a water-resistant (e.g., water-fast) printed image on paper by applying a colorant to the ink-jet recording medium according to the invention, where the colorant contains reactive

ionizable and/or nucleophilic groups capable of reacting with at least one coating agent in one or more of the layers of the ink-jet recording medium.

In general, aqueous inks are used in the preparation of a printed image on the ink-jet recording medium of the invention. The aqueous ink may be any suitable ink having a colorant, e.g., a pigment, dye, or stain, having one or more reactive groups suitable for reacting, either covalently or ionically, with a colorant-reactive component of the coating agent present on the coated paper substrate. The selection of the specific ink and colorant will vary with the colorant-reactive component of the coating agent used in coating the ink-jet medium. For example, when the colorant-reactive component is an azetidinium group, the colorant preferably has a nucleophilic group for reaction with the azetidinium group. Thus, preferred colorants for use in printing on a coated paper substrate having an azetidinium polymer in the polymer coating are those containing one or more nucleophilic moieties, e.g., having an amino, carboxy, sulfonato, thiosulfonato, cyano, hydroxy or sulfido group or the like. Preferred colorants for use in printing a paper substrate coated with a guanidine polymer are those containing an anionic group, e.g., having a carboxy, sulfonato, thiosulfonato, cyano, halo, or phosphonato group or the like.

The inks used in conjunction with the coated paper substrate of the invention may be inkjet inks. Water-soluble colorants in the inkjet inks may be acid dyes, direct dyes, basic dyes or dispersive dyes; preferred dyes for use in the invention are described in U.S. Pat. Nos. 5,425,805, 5,537,137, and 5,441,561.

The selection of the aqueous based ink will depend upon the requirements of the specific application, such as desired surface tension, viscosity, drying time, the type of paper substrate upon which the ink is to be applied (printing medium), and the like. The aqueous liquid vehicle of inks suitable for use in the invention will generally be deionized water, although other nonorganic compounds which are either water soluble or water miscible may be included as well. The colorant may be dissolved, dispersed or suspended in the aqueous liquid vehicle, and is present in an amount effective to provide the dried ink with the desired color and color intensity.

In some instances, the dye is contained in a carrier medium composed of ink and a water soluble organic solvent. For applications utilizing such a carrier medium, representative solvents include polyols such as polyethylene alcohol, diethylene glycol, propylene glycol, and the like. Additional solvents are simple alcohols such as ethanol, isopropanol and benzyl alcohol, and glycol ethers, e.g., ethylene glycol monomethyl ether, diethylene glycol monoethyl ether. Representative examples of water soluble organic solvents are described in U.S. Pat. No. 5,085,698 and U.S. Pat. No. 5,441,561.

Preferred colorants contained in the inks useful with the invention are dyes, including azo or "direct" dyes as well as dyes containing acidic groups (e.g., carboxylate, phosphonate or sulfonate moieties), basic groups (e.g., unsubstituted amines or amines substituted with 1 or 2 alkyl, typically lower alkyl, groups), or both. Specific examples of suitable colorants include, but are not limited to, the following: Dispersol Blue Grains (Zeneca, Inc.), Duasyn Acid Blue (Hoechst Celanese), Duasyn Direct Turquoise Blue (Hoechst Celanese), Phthalocyanine blue (C.I. 74160), Diane blue (C.I. 21180), Pro-jet Cyan 1 (Zeneca, Inc.), Pro-jet Fast Cyan 2 (Zeneca, Inc.), Milori blue (an inorganic pigment equivalent to ultramarine) as cyan colorants; Dispersol Red D-B Grains (Zeneca, Inc.), Brilliant carmine 6B (C.I. 15850), Pro-jet magenta 1 (Zeneca, Inc.), Pro-jet Fast magenta 2 (Zeneca, Inc.), Brilliant Red F3B-SF (Hoechst Celanese), Red 3B-SF (Hoechst Celanese), Acid Rhodamine (Hoechst Celanese), Quinacridone magenta (C.I. Pigment Red 122) and Thioindigo magenta (C.I. 73310) as magenta colorants; Dispersol Yellow D-7G 200 Grains (Zeneca, Inc.), Brilliant yellow (Hoechst Celanese), Pro-jet yellow 1 (Zeneca, Inc.), Pro-jet Fast Yellow 2 (Zeneca, Inc.), benzidine yellow (C.I. 21090 and C.I. 21100) and Hansa Yellow (C.I. 11680) as yellow colorants; organic dyes; and black materials such as carbon black, charcoal and other forms of finely divided carbon, iron oxide, zinc oxide, titanium dioxide, and the like. Specific and preferred black colorants include Acid Black 48 (Aldrich), Direct Black 58756 A (Crompton & Knowles), BPI Molecular Catalytic Gray (Brain Power), Fasday Cool Gray (Hunter Delator), Dispersol Navy XF Grains (Zeneca, Inc.), Dispersol Black CR-N Grains (Zeneca, Inc.), Dispersol Black XF Grains (Zeneca, Inc.), Disperse Black (BASF), Color Black FW18 (Degussa), Color Black FW200

(Degussa), Hostafine Black TS (Hoechst Celanese), Hostafine Black T (Hoechst Celanese), Duasyn Direct Black (Hoechst Celanese), Pro-jet Black 1 (Zeneca, Inc.) and Pro-jet Fast Black 2 (Zeneca, Inc.).

Printed Ink-jet Recording Medium

The invention also features a printed, ink-jet recording medium which is a coated paper substrate produced as described herein. The printed, ink-jet recording medium of the invention can be produced by any of a variety of printing techniques, including inkjet printing, laserjet printing, photocopying, and the like. In general, the printing process involves applying an aqueous recording liquid to a coated paper substrate in an image-wise pattern. Inkjet printing processes are well known in the art; see, e.g., U.S. Pat. Nos. 4,601,777; 4,251,824; 4,410,899; 4,412,224; and 4,532,530.

The ink-jet recording medium of the invention can also be used in printing and/or copying process using dry or liquid electrophotographic-type developers, such as electrophotographic processes, ionographic process, and the like. The coated paper substrates of the invention can in addition be used in a process for generating images that involves generating an electrostatic latent image on an imaging member in an imaging apparatus, developing the latent image with a toner, and transferring the developed image to a coated paper substrate of the invention. Electrophotographic processes are known in the art, see, e.g., U.S. Pat. No. 2,297,691. Ionographic and electrographic processes are also well known in the art, see, e.g., U.S. Pat. Nos. 3,611,419; 3,564,556; 4,240,084; 4,569,584; 2,919,171; 4,524,371; 4,619,515; 4,463,363; 4,254,424; 4,538,163; 4,409,604; 4,408,214; 4,365,549; 4,267,556; 4,160,257; and 4,155,093.

The ink-jet recording medium of the invention can also be used in any other printing or imaging process, such as printing with pen plotters, handwriting with ink pens (either aqueous or nonaqueous based inks), offset printing processes, and the like.

Experimental

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to prepare and

use the compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in .degree. C. and pressure is at or near atmospheric.

Examples of Coating Compositions

Example-1

Poly alkyl oxazoline homopolymer (10wt%)----------25 parts
Silicagel pigment dispersions(40wt%)----------20 parts
Cross linkable acrylic latex dispersions(~25wt%)----------30 parts
Polymethyl acrylate trimethyl ammonium chloride(~35wt%)-----8parts
Alumina pigment dispersions (30wt%)----------15parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactans and plasticizes and other additives----------1 part

Example-2

Poly alkyl oxazoline homopolymer (10wt%)----------30 parts
Cross linkable acrylic latex dispersions(~25wt%)---------20 parts
Polymethyl acrylate trimethyl ammonium chloride(~35wt%)-----35parts
Alumina pigment dispersions (30wt%)----------12parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Example-3

Poly alkyl oxazoline homopolymer (10wt%)----------10 parts
Cross linkable acrylic latex dispersions(~25wt%)---------20 parts
Polymethyl acrylate trimethyl ammonium chloride(~35wt%)-----60parts
Silica pigment dispersions (40wt%)----------5parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Example-4

Poly alkyl oxazoline homopolymer (10wt%)----------10 parts

Ethylene –polyvinyl acetate(~40wt%)----------20 parts
Polymethyl acrylate trimethyl ammonium chloride(~35wt%)-----60parts
Alumina pigment dispersions (40wt%)----------5parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Example-5

Poly alkyl oxazoline homopolymer (10wt%)----------10 parts
Ethylene –polyvinyl acetate(~40wt%)----------20 parts
Cross linkable acrylic latex dispersions(~25wt)-------10
Polymethyl acrylate- trimethyl ammonium chloride(~35wt%)-----50parts
Silica pigment dispersions(40wt%)----------5parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Example 6

Polyvinylalcohol (10wt%)----------30 parts
Ethylene –polyvinyl acetate(~40wt%)----------25 parts
Cross linkable acrylic latex dispersions(~25wt)-------17 parts
Copolymer of Polyvinyl caprolactam and aminoacrylate(~35wt%)-----20parts
Silica pigment dispersions(40wt%)----------5parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Example 7

Polyvinylalcohol (10wt%)----------15 parts
Polyhydroxyethylmethacrylate acrylic acid copolymer (~20wt%)----------30 parts
Polyvinyl pyrrolidone homopolymer-(10%)--------10 parts
Cross linkable acrylic latex dispersions(~25wt)-------17 parts
Copolymer of Polyvinyl caprolactam and aminoacrylate(~35wt%)-----20parts
Silica pigment dispersions(40wt%)----------5parts
Polyamino amide- epichlorohydrine adduct (12.5wt%)----------2parts
Surfactants and plasticizers and other additives----------1 part

Typical Product Examples and Procedures

Coated Product Example 1

The layer made of the composition of Example 1 is layed on the substrate (canvas, glossy substrate, metallized substrate) using a Myer Rod #30 and the coating is dried in the oven ~80 degrees for a few minutes

Results - The coated and dried substrates produce high gloss (~90) and when printed with ink jet printers produced bright colors and water fast prints.

Without further description, it is believed that one of ordinary skill in the art can, using the preceding description, make and utilize the compositions of the present invention and practice the claimed methods. The examples of coating compositions and methods as well as their proportions, specifically point out preferred embodiments of the present invention, and are not to be construed as limiting in any way the remainder of the disclosure. Such examples are non-limiting in that one of ordinary skill (in view of the above) will readily envision other permutations and variations on the invention without departing from the principal concepts. Such permutations and variations are also within the scope of the present invention.

Claims

What is claimed is:

1. An ink jet or commercial graphic recording media system that comprises a support and one or more coating layers thereon, wherein at least one coating layer comprises:

(a) a polyalkyloxazoline homopolymer at a weight percent from 5% to 35%

(b) a member selected from a cross-linkable latex dispersion and ethylene-polyvinyl acetate at a weight percent from 10% to 70%, and

(c) a member selected from polymethyl acrylate trimethylammonium chloride at a weight percent from 10% to 60% and polyhydroxyethylmethacrylate-polyacrylic acid copolymer 10-40%.

2. A recording media system according to claim 1, further comprising one or more of the following:

(i) one or more members selected from polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, polymeric cyclic amides as homopolymers or copolymers of cylic amides and amino acrylates, polycaprolactams, copolymers of hydroxymethylethacrylates and aminoacrylates and the corresponding salts of amino moiety of the copolymer, and terpolymers of hydroxyethylmethacrylates, aminoacrylates, acrylic acids and their amino salts at a weight percent from 10% to 35%

(ii) polyvinyl alcohols 10-35%

(iii) polyvinyl pyrrolidones 10-20%, and

(iv) polyamino amide epichlorohydrine adduct at a weight percent from 1% to 5%.

3. A recording media system according to claim 1, optionally further containing pigment dispersions, surfactants and other additives at a weight percent from 10 to 45%.

4. A recording media system according to claim 3, wherein one or more of the coating layers comprises one or more pigments, fillers or organic particulates selected from the group consisting of amorphous silica, crystalline silica, aluminum trihydrate, kaolin, talcum, chalk, betonite, zeolite, glass beads, calcium carbonate, potassium sodium aluminum silicate, diatomaceous earth, silicates of aluminum, silicates of magnesium, titanium doxide, polyolefins, polystyrene, polyurethane, starch, poly(methyl methacrylate) and polytetrafluoroethylene.

5. A recording media system according to claim 3, wherein the pigment dispersion is present at a weight percent from 15% to 45%.

6. A recording media system according to claim 5, wherein the pigment dispersion is a silica pigment dispersion, an alumina pigment dispersion, or a mixture thereof.

7. A recording media system according to claim 1, wherein one or more of the coating layers comprises an ink jet receptive layer.

8. A recording media system according to claim 6, which further comprises a barrier layer between the support and the ink receptive layer or layers.

9. A recording media system according to claim 1 wherein one or more of the coating layers further comprises ink jet ink.

10. A recording media system according to claim 1 which further comprises one or more additives selected from the group consisting of surface active agents, antistatic agents, thickeners, suspending agents, pH controlling compounds, light stabilizers, antioxidants, humectants, bacteriostats, crosslinking agents and optical brighteners, flavor agents

11. A recording media system according to claim 10 in which the additives are selected from the group consisting of phenolic antioxidants,

hydroxybenzotriazole ultraviolet light absorbers, benzophenone ultraviolet light absorbers, hydroxyphenyltriazine ultraviolet light absorbers and hindered amine light stabilizers.

12. A recording media system according to claim 1 in which said support comprises cellulose, cellulose esters, cellulose acetate, polyesters, polystyrene, polyethylene, poly(vinyl acetate), polypropylene, polycarbonate, polymethacrylic acid and methyl and ethyl esters, polyamides such as nylons, polyesters such as poly(ethylene terephthalate) (PET), polyimides, polyethers, polyvinyl chloride polytetrafluoroethylene, polyvinylidene fluoride or polysulfonamides.

13. A recording media system according to claim 1 in which said support is paper or transparent poly(ethylene) terephthalate.

14. A recording media system according to claim 12 in which said support is a fabric such as a cloth, canvas, or other similar flexible support.

15. A method for preparing an ink jet recording media system, which method comprises applying one or more coating layers on a support, wherein at least one of the coating layers is a coating layer according to the media system of claim 1.

16. A substrate support for ink jet recording comprising the ink jet recording media system of claim 1.

17. A substrate support for ink jet recording according to claim 16, wherein said substrate support comprises cellulose, cellulose esters, cellulose acetate, polyesters, polystyrene, polyethylene, poly(vinyl acetate), polypropylene, polycarbonate, polymethacrylic acid and methyl and ethyl esters, polyamides such as nylons, polyesters such as poly(ethylene terephthalate) (PET), polyimides, polyethers, polyvinyl chloride polytetrafluoroethylene, polyvinylidene fluoride or polysulfonamides.

18. A substrate support for ink jet recording according to claim 16 in which said support is paper or transparent poly(ethylene) terephthalate, metal deposited foil substrate of various colors

19. A substrate support recording media system according to claim 17 in which said support is a fabric such as a cloth, canvas, or other similar flexible support.