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(54) Title: INKJET RECORDING ELEMENT

(57) Abstract: An inkjet recording element comprising a support having thereon, in order over a support, a base layer comprising a synthetic or natural polymer and optionally a polymeric mordant; an inner layer comprising acetoacetylated or carboxylated poly(vinyl alcohol); and an overcoat comprising poly(vinyl alcohol) binder and particles of a synthetic, substantially amorphous aluminosilicate material. Such recording elements exhibit improved adhesion during printing.



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INKJET RECORDING ELEMENT

FIELD OF THE INVENTION

The present invention relates to an inkjet recording element and a
5 printing method using the element.

BACKGROUND OF THE INVENTION

In a typical inkjet 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
10 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.

An ink-recording element typically comprises a support having on
at least one surface thereof one or more ink-receiving or image-forming layers,
15 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.

In order to achieve and maintain high quality images on such an
inkjet recording element, the recording element must exhibit no banding, bleed,
20 coalescence, or cracking in inked areas; exhibit the ability to absorb large amounts
of ink and dry quickly to avoid blocking; exhibit high optical densities in the
printed areas; exhibit freedom from differential gloss; exhibit high levels of image
fastness to avoid fade from contact with water or radiation by daylight, tungsten
light, fluorescent light, or exposure to gaseous pollutants; and exhibit excellent
25 adhesive strength so that delamination does not occur.

U.S. Patent Application Serial Number _____ by Richard J.
Kapusniak et al. (Docket 87532) titled "Inkjet Recording Element Comprising
Subbing Layer and Printing Method" discloses a subbing layer comprising an
allophane-like aluminosilicate in an inner layer for improved adhesion.

30 The use of aluminosilicate particles to increase smudge resistance
in an overcoat is disclosed in U.S. Serial Number 10/705,057 by Charles E.

Romano, Jr. et al., titled "Ink Jet Recording element and Printing Element" filed November 10, 2003, hereby incorporated by reference in its entirety.

U.S. Patent No 6,341,560 issued January 29, 2002 to Shah et al., titled "Imaging And Printing Methods Using Clay-containing Fluid Receiving Element," discloses a lithographic imaging member that is prepared by applying
5 an ink-jetable fluid to a fluid-receiving element that includes a clay-containing fluid-receiving surface layer. Useful clays that are used are either synthetic or naturally occurring materials, including but not limited to kaolin (aluminum silicate hydroxide) and many other clays such as serpentine, montmorillonites,
10 illites, glauconite, chlorite, vermiculites, bauxites, attapulgites, sepiolites, palygorskites, corrensites, allophanes, imogolites, and others.

Aluminosilicates are known in various forms. For example aluminosilicate polymers are known in fiber form, such as imogolite. Imogolite is a filamentary, tubular and crystallized aluminosilicate, present in the impure
15 natural state in volcanic ashes and certain soils; it was described for the first time by Wada in Journal of Soil Sci. 1979, 30(2), 347-355. In comparison, allophanes are in the form of substantially amorphous particles.

Naturally occurring allophane is a series name used to describe clay-sized, short-range ordered aluminosilicates associated with the weathering of
20 volcanic ashes and glasses. Such natural allophane commonly occurs as very small rings or spheres having diameters of approximately 35 - 50 Å (3.5 to 5.0 nm). This morphology is characteristic of allophane, and can be used in its identification. Naturally occurring allophanes have a composition of approximately $\text{Al}_2\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$. Some degree of variability in the Si:Al ratios is
25 present. Wada reports Si:Al ratios varying from about 1:1 to 2:1. Because of the exceedingly small particle size of allophane and the intimate contact between allophane and other clays (such as smectites, imogolite, or non-crystalline Fe and Al oxides and hydroxides and silica) in the soil, it has proven very difficult to accurately determine the composition of naturally occurring allophane. Allophane
30 usually gives weak XRD peaks at 2.25 and 3.3 Å. Identification is commonly made by infrared analyses or based on transmission electron morphology.

A limited amount of isomorphous substitution occurs in natural allophane. The most common type is the substitution of Fe for Al. In some cases, the color of this natural allophane is dark yellow due to the presence of Fe³⁺, the presence of which can interfere with making Raman spectrum of the natural
5 allophane due to the presence of this Fe³⁺ traces (fluorescence under the laser excitation). Little permanent charge is typically present in natural allophane. The majority of the charge is variable charge, and both cation and anion exchange capacities exist, with the relative amounts depending on the pH and ionic strength of the soil chemical environment of the natural allophane.

10 In contrast, the zeta potential of synthetic allophane is positive, which is in the range of other pure alumina materials. Synthetic allophane, however, like natural allophane, is also a substantially amorphous material having weak XRD signals. The particle size (average diameter) typically is in the range of about 4 to 5.5 nm. Due to their small size, it is difficult to obtain a photo of a
15 single unit of synthetic allophane, but they commonly appear substantially spherical, which spheres are usually hollow. There is data supporting the chemical anisotropy of synthetic allophane, with aluminols at the outer surface, silanols wrapping the inner surface.

Aluminosilicate polymers, in spherical particle form, that can be
20 described as synthetic allophanes are disclosed in U.S. Patent No. 6,254,845 issued July 3, 2001 to Ohashi et al., titled "Synthesis Method Of Spherical Hollow Aluminosilicate Cluster," which patent describes an improved method for preparing hollow spheres of amorphous aluminosilicate polymer similar to natural allophane. This patent also refers to Wada, S., Nendo Kagaku (Journal of the
25 Clay Science Soc. of Japan), Vol. 25, No. 2, pp. 53-60, 1985) for another synthesis of amorphous aluminosilicate superfine particles. The aluminosilicate polymers in US-A-6,254,845 to Ohashi et al. are within a range of 1-10 nm, shaped as hollow spheres, and are observed to form hollow spherical silicate "clusters" or aggregates in which pores are formed. The patent to Ohashi et al. states that
30 powder X-ray diffraction reveals two broad peaks close to 27° and 40° at 2θ on the Cu-K_α line, which correspond to a non-crystalline (substantially amorphous)

structure and which is characteristic of spherical particles referred to as allophane. In addition, observations under a transmission microscope reveal a state in which hollow spherical particles with diameters of 3-5 nm are evenly distributed.

Regarding the Al/Si ratio, it is believed that sufficient silanol group
5 is needed to form an homogeneous layer of silicate on the face of the proto gibbsite sheet, sufficient to curl this protogibbsite sheet and finally allowing a closo structure to be obtained. The Al/Si ratio, therefore, has to be in the range 1 to 4.

Two types of synthetic allophane, referred to as hybrid and
10 classical, are disclosed in French Applications FR 0209086 and FR 0209085 filed on July 18, 2002. Hybrid Synthetic allophanes show the same fingerprints as classical allophane with some additional bands due to the presence of organic groups.

As indicated above, synthetic and natural allophane are generally
15 non-crystalline materials, which include both amorphous and short-range ordered materials such as microcrystalline materials. Amorphous materials are at the opposite extreme from crystalline materials -- they do not have a regularly repeating structure, even on a molecular scale. Their compositions may be regular or, as is more commonly the case, they may have a large degree of variability.
20 They do not produce XRD peaks. Since the term amorphous is sometimes applied to materials that are truly amorphous, like volcanic glass, the term x-ray amorphous or simply non-crystalline can be used to describe allophanes and other short-range ordered materials that may show weak XRD peaks and hence not completely amorphous. Such aluminosilicate materials will be referred to herein
25 as substantially amorphous. Short-range ordered materials can sometimes be identified by XRD or selective dissolution in conjunction with differential XRD.

While a wide variety of different types of image recording elements for use with ink printing are known, there are many unsolved problems in the art and many deficiencies in the known products, which have severely limited their
30 commercial usefulness. A major challenge in the design of an image-recording element is laminate adhesion. U.S. Pat. Nos. 5,942,335 and 5,856,023 disclose an

ink-receiving layer which is a mixture of derivatized and underivatized poly(vinyl alcohol). The layer may also contain poly(vinylbenzyl quaternary ammonium salt) with or without polyvinylpyrrolidinone. U.S. Pat. Nos. 6,010,790 and 6,068,373 disclose an ink receiving layer comprising a hydrophilic polymer, preferably
5 poly(vinyl alcohol) and poly(vinylbenzyl quaternary ammonium salt) and optionally containing derivatized and underivatized poly(vinyl alcohol). Acetoacetylated poly(vinyl alcohol) is disclosed as a single ink receiving layer in U.S. Pat. Nos. 6,020,398, 6,074,057, 6,137,514, 6,161,929, 6,206,517, 6,224,202, and 6,276,791. U.S. Pat. No. 6,224,971 discloses acetoacetylated
10 poly(vinyl alcohol) in combination with polyvinylpyrrolidinone resin and an acidic aqueous dispersion of colloidal silica.

US 2003/157276 A1 to Romano, Jr. et al. discloses an inkjet recording element comprising a support having a hydrophilic absorbing layer, preferably, and a laminate-adhesion-promoting overcoat polymer layer comprising
15 a derivatized poly(vinyl alcohol) having at least one hydroxyl group replaced by ether or ester groupings, preferably comprising acetoacetylated poly(vinyl alcohol) and a polyurethane dispersion wherein the weight ratio of derivatized poly(vinyl alcohol) to polyurethane dispersion is between 50:50 and 95:5.

It is an object of this invention to provide a multilayer inkjet
20 recording element that has excellent image quality and improved interlayer adhesion.

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

SUMMARY OF THE INVENTION

25 These and other objects are achieved by the present invention which comprises an inkjet recording element comprising at least three non-porous (swellable) hydrophilic absorbing layers and which exhibit improved interlayer adhesion, excellent image quality, and extended print life.

In particular, the inkjet recording element of the present invention
30 comprising, in order over a support, at least three hydrophilic absorbing layers, namely (a) a base layer comprising a synthetic or natural polymer and optionally a

mordant; (b) a non-porous inner layer comprising a acetoacetylated poly(vinyl alcohol) or a carboxylated poly(vinyl alcohol); and (c) an overcoat comprising poly(vinyl alcohol) binder and particles of a synthetic, substantially amorphous aluminosilicate material. The order is such that the inner layer is between the base layer and the overcoat, and the base layer is the closest of the three layers to the support.

In a preferred embodiment of the invention, the ratio of hydrophilic polymer to the aluminosilicate particles in both the overcoat and the inner layer is about from about 97.5:2.5 to about 75:25. In another preferred embodiment the base layer comprises gelatin and a cationic polymeric mordant.

Another embodiment of the invention relates to an inkjet printing method comprising the steps of: A) providing an inkjet printer that is responsive to digital data signals; B) loading the inkjet printer with the inkjet recording element described above; C) loading the inkjet printer with an inkjet ink; and D) printing on the inkjet recording element using the inkjet ink in response to the digital data signals.

As used herein, the terms "over," "above," "under," and the like, with respect to layers in the inkjet media, refer to the order of the layers over the support, but do not necessarily indicate that the layers are immediately adjacent or that there are no intermediate layers.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the inkjet recording element comprises at least three hydrophilic absorbing (swellable non-porous) layers each of which comprises independently a natural or synthetic polymer as binder.

The hydrophilic absorbing layers must effectively absorb both the water and humectants commonly found in printing inks as well as the recording agent (typically dyes). The inner layer, the base layer, the overcoat layer, and any other hydrophilic absorbing layers will collectively be referred to as the hydrophilic absorbing layers, the layers cumulatively capable of effectively absorbing the ink composition including liquid carrier upon application by an inkjet printer. The ink colorant or image-forming portion of the ink may form a

gradient and may be present, to at least some degree in all three hydrophilic absorbing layers, typically forming a colorant or dye gradient. However, due to the location of the mordant and the thickness of the layers, the base layer is intended to receive and contain most of the colorant, preferably more than 70% by weight of the applied colorant employing a typical inkjet dye-based composition.

In one embodiment of the invention, the hydrophilic absorbing layers comprise a first hydrophilic absorbing layer, a base layer comprising gelatin, and at least one upper layer or second hydrophilic absorbing layer (also referred to as the "inner layer"), located between the base layer and an overcoat layer comprising poly(vinyl alcohol). These embodiments provide enhanced image quality.

Preferred binders for the hydrophilic absorbing layers comprise gelatin, poly (vinyl alcohol) (PVA), and acetoacetylated or carboxylated poly(vinyl alcohol). The layers, however, may also optionally contain, for example, additional other hydrophilic materials such as naturally-occurring hydrophilic colloids and gums such as gelatin or modified gelatin, albumin, guar, xanthan, acacia, chitosan, starches and their derivatives, functionalized proteins, functionalized gums and starches, and cellulose ethers and their derivatives, polyvinylloxazoline, such as poly(2-ethyl-2-oxazoline) (PEOX), polyvinylmethyloxazoline, polyvinylmethyloxazoline, polyoxides, polyethers, poly(ethylene imine), poly(acrylic acid), poly(methacrylic acid), n-vinyl amides including polyacrylamide and polyvinyl pyrrolidinone (PVP), and other poly(vinyl alcohol) derivatives and copolymers, such as copolymers of poly(ethylene oxide) and poly(vinyl alcohol) (PEO-PVA), polyurethanes, and polymer latices such as polyesters and acrylates. Derivatized poly(vinyl alcohol) includes, but is not limited to, polymers having at least one hydroxyl group replaced by ether or ester groups, for example, an acetoacetylated poly(vinyl alcohol) in which the hydroxyl groups are esterified with acetoacetic acid. A copolymer of poly(vinyl alcohol), for example, is carboxylated PVA in which an acid group is present in a comonomer. More than one polymer may be present in a layer.

A preferred binder for the base layer is gelatin, which is preferably made from animal collagen, especially gelatin made from pig skin, cow skin, or cow bone collagen due to ready availability. This kind of gelatin is not specifically limited, but lime-processed gelatin, acid processed gelatin, amino group inactivated gelatin (such as acetylated gelatin, phthaloylated gelatin, malenoylated gelatin, benzoylated gelatin, succinylated gelatin, methyl urea gelatin, phenylcarbamoylelated gelatin, and carboxy modified gelatin), or gelatin derivatives (for example, gelatin derivatives disclosed in JP Patent publications 38-4854/1962, 39-5514.1964, 40-12237/1965, 42-26345/1967, and 2-13595/1990; U.S. Patents 2,525,753, 2,594,293, 2,614,928, 2,763,639, 3,118,766, 3,132,945, 3,186,846, 3,312,553; and GB Patents 861,414 and 103, 189) can be used singly or in combination. Most preferred are pigskin or modified pigskin gelatins and acid processed osseine gelatins due to their effectiveness for use in the present invention.

As noted above, the poly(vinyl alcohol) employed in the invention, at least in the overcoat, has a degree of hydrolysis of at least about 50% and has a number average molecular weight of at least about 45,000. In a preferred embodiment of the invention, the poly(vinyl alcohol) has a degree of hydrolysis of about 70 to 99%, more preferably about 75 to 90%. Commercial embodiments of such a poly(vinyl alcohol) include Gohsenol ® AH-22, Gohsenol ® AH-26, Gohsenol ® KH-20, and Gohsenol ® GH-17 from Nippon Gohsei and Elvanol®52-22 from DuPont (Wilmington, DE).

According to the present invention, as indicated above, the inner layer comprises a derivitized or copolymerized poly(vinyl alcohol) selected from the group acetoacetylated and carboxylated poly(vinyl alcohol), or combinations thereof. The derivitized poly(vinyl alcohol) has at least one hydroxyl group replaced by ester groups, preferably an acetoacetylated poly(vinyl alcohol) in which the hydroxyl groups are esterified with acetoacetic acid. Preferably the derivitized poly(vinyl alcohol) has an average molecular weight of from 15,000 to 150,000, a saponification degree (mol%) of from 80 - 100%, and a modification

degree (mol%) of from 2.5 - 15%. These derivitized poly(vinyl alcohol) compounds are readily available from various commercial suppliers.

Carboxylated polyvinyl alcohols include copolymers of vinyl alcohol and ethylenically unsaturated monobasic carboxylic acids, such as crotonic or isocrotonic acid, or acrylic or methacrylic acid. The carboxylated polyvinyl alcohols preferably have a viscosity of 20 to 50 mPa in a 4% aqueous solution at room temperature. The average molecular weight preferably is 5,000 to 20,000, more preferably 7,000 to 10,000. Examples of commercially available a carboxylated polyvinyl alcohol is, for example, Gohsenol T-330 manufactured by Nippon Synthetic Chemical Industry Co., Ltd. of Osaka, Japan, and distributed in the United States by Marubeni American Corporation of New York. Other carboxylated polyvinyl alcohol compounds which may be used with the present invention include Gohsenol T-350, OKS-3381 and OKS-3382 also manufactured by the Nippon Synthetic Chemical Industry Co., Ltd.

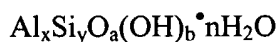
The dry layer thickness of the inner layer is preferably from 0.5 to 10 μm (more preferably 1 to 5 microns). The preferred dry coverage of the overcoat layer is from 0.5 to 5 μm (more preferably 0.5 to 1.5 microns) as is common in practice. The dry layer thickness of the base layer is preferably from 5 to 60 microns (more preferably 6 to 15 microns), below which the layer is too thin to be effective and above which no additional gain in performance is noted with increased thickness. In a preferred embodiment of the invention, the ratio of the thickness of the base layer (of the dried coating) to that of both the inner layer and overcoat is at least 2.5 to 1, preferably at least 3.5 to 1, more preferably between 4:1 and 10:1. In one preferred embodiment, the ratio is between 5:1 and 7:1. With respect to such ratios, each layer may or may not be divided and comprise one or more sub-layers.

The binder for the overcoat, in addition to the poly(vinyl alcohol) can optionally include any of the polymers mentioned above for the hydrophilic absorbing layers. This layer may also contain other hydrophilic materials such as cellulose derivatives, e.g., cellulose ethers like methyl cellulose (MC), ethyl cellulose, hydroxypropyl cellulose (HPC), sodium carboxymethyl cellulose

(CMC), calcium carboxymethyl cellulose, methylethyl cellulose, methylhydroxyethyl cellulose, hydroxypropylmethyl cellulose (HPMC), hydroxybutylmethyl cellulose, ethylhydroxyethyl cellulose, sodium carboxymethyl-hydroxyethyl cellulose, and carboxymethylethyl cellulose, and
5 cellulose ether esters such as hydroxypropylmethyl cellulose phthalate, hydroxypropylmethyl cellulose acetate succinate, hydroxypropyl cellulose acetate, esters of hydroxyethyl cellulose and diallyldimethyl ammonium chloride, esters of hydroxyethyl cellulose and 2-hydroxypropyltrimethylammonium chloride and esters of hydroxyethyl cellulose and a lauryldimethylammonium substituted
10 epoxide (HEC-LDME), such as Quatrisoft® LM200 (Amerchol Corp.) as well as hydroxyethyl cellulose grafted with alkyl C₁₂-C₁₄ chains. The overcoat is non-porous. Optionally, particles or beads, inorganic or organic, can be present in the overcoat in an amount up to about 40 weight percent total solids. Such particles can be used for various purposes, to increase solids, to provide a matte finish, as a
15 filler, as a viscosity reducer, and/or to increase smudge resistance.

The overcoat can comprises from about 2.5 to 30 percent by weight solids of particles of a synthetic aluminosilicate material, preferably about 5 to 20 percent of the overcoat solids. The preferred aluminosilicate is similar to natural allophane, but is a synthetically produced material not derived from a natural or
20 purified natural aluminosilicate material and that is substantially amorphous. In one embodiment the particles are in the form of spheres or rings, preferably substantially spherical spheres 1 to 10 nm in average diameter, as observable under an electron microscope. The primary particles can be in the form of clusters of primary particles.

25 In a preferred embodiment of the invention, the aluminosilicate material (in either the overcoat or inner layer or both layers) has the formula:



where the ratio of x:y is between 0.5 and 4, a and b are selected such that the rule of charge neutrality is obeyed; and n is between 0 and 10.

In a more preferred embodiment, the aluminosilicate has the formula:



where the ratio of x:y is between 1 and 3.6, preferably 1 to 3, more preferably 1 to 2, and a and b are selected such that the rule of charge neutrality is obeyed; and n is between 0 and 10. More preferably, it is a substantially amorphous aluminosilicate, spherical or ring shaped, with a general molar ratio of Al to Si not more than 2:1.

The preferred polymeric aluminosilicate can be obtained, for example, by the controlled hydrolysis by an aqueous alkali solution of a mixture of an aluminum compound such as halide, perchloric, nitrate, sulfate salts or alkoxides species $\text{Al}(\text{OR})_3$, and a silicon compound such as alkoxides species, wherein the molar ratio Al/Si is maintained between 1 and 3.6 and the alkali/Al molar ratio is maintained between 2.3 and 3. Such materials are described in French patent application FR 02/9085, hereby incorporated by reference in its entirety.

A polymeric aluminosilicate can also be obtained by the controlled hydrolysis by an aqueous alkali solution of a mixture of an aluminum compound such as halide, perchloric, nitrate, sulfate salts or alkoxides species $\text{Al}(\text{OR})_3$ and a silicon compound made of mixture of tetraalkoxide $\text{Si}(\text{OR})_4$ and organotrialkoxide $\text{R}'\text{Si}(\text{OR})_3$, wherein the molar ratio is maintained between 1 and 3.6 and the alkali/Al molar ratio is maintained 2.3 and 3. Such materials are described in French patent application FR 02/9086, hereby incorporated by reference in its entirety.

Synthetic hollow aluminosilicates are disclosed in U.S. Patent No. 6,254,845 issued July 3, 2001 to Ohashi et al., titled "Synthesis Method Of Spherical Hollow Aluminosilicate Cluster," hereby incorporated by reference. As mentioned earlier, the method used therein results in a synthetic allophane in which powder X-ray diffraction reveals two broad peaks close to 27° and 40° at 2θ on the Cu-K_α line, which correspond to a non-crystalline (substantially amorphous) structure and which is characteristic of spherical particles referred to

as allophane. In some cases, allophanes have also been characterized as giving weak XRD peaks at least at about 2.2 and 3.3. The method of synthesis may affect the XRD pattern, however, and depending on the preparation, additional peaks may be present at about 7.7 to 8.4 Å and/or about 1.40 Å.

5 The aluminosilicate of the present invention can include, but is not limited to, materials termed "synthetic allophane" or "allophane like." Synthetic allophane is typically in the form of substantially spherically or ring shaped aluminosilicate particles, including hollow spherical aluminosilicate particles, preferably having an average diameter of between 3.5 and 5.5 nm. In addition,
10 synthetic allophanes, like natural allophanes, are substantially amorphous (P. Bayliss, Can. Mineral. Mag., 1987, 327), compared to, for example, imogolites which are crystalline and fibril shaped. Synthetic allophane differs from natural allophane (such as Allophosite® sold by Sigma) in that it does not contain iron. It may also be more amorphous and acidic.

15 In more detail, a preferred method for preparing an aluminosilicate polymer comprises the following steps:

(a) treating a mixed aluminum and silicon alkoxide only comprising hydrolyzable functions, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon
20 compounds only comprising hydrolyzable functions, with an aqueous alkali, in the presence of silanol groups, the aluminum concentration being maintained at less than 1.0 mol/l, the Al/Si molar ratio being maintained between 1 and 3.6 and the alkali/Al molar ratio being maintained between 2.3 and 3;

(b) stirring the mixture resulting from step (a) at ambient
25 temperature in the presence of silanol groups long enough to form the aluminosilicate polymer; and

(c) eliminating the byproducts formed during steps (a) and (b) from the reaction medium.

The expression "hydrolyzable function" means a substituent
30 eliminated by hydrolysis during the process and in particular at the time of treatment with the aqueous alkali. The expression "unmodified mixed aluminum

and silicon alkoxide" or "unmodified mixed aluminum and silicon precursor" means respectively a mixed aluminum and silicon alkoxide only having hydrolyzable functions, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon compounds only having hydrolyzable functions. More generally, an "unmodified" compound is a compound that only comprises hydrolyzable substituents.

Step (c) can be carried out according to different well-known methods, such as washing or diafiltration.

The aluminosilicate polymer material obtainable by the method defined above has a substantially amorphous structure shown by electron diffraction. This material is characterized in that its Raman spectrum comprises in spectral region 200-600 cm^{-1} a wide band at $250 \pm 6 \text{ cm}^{-1}$, a wide intense band at $359 \pm 6 \text{ cm}^{-1}$, a shoulder at $407 \pm 7 \text{ cm}^{-1}$, and a wide band at $501 \pm 6 \text{ cm}^{-1}$, the Raman spectrum being produced for the material resulting from step (b) and before step (c).

Alternatively, hybrid aluminosilicate polymers involving the introduction of functions, in particular organic functions into the inorganic aluminosilicate polymer enables a hybrid aluminosilicate polymer to be obtained in comparison to inorganic aluminosilicate polymers. A method for preparing a hybrid aluminosilicate polymer, comprises the following steps:

(a) treating a mixed aluminum and silicon alkoxide of which the silicon has both hydrolyzable substituents and a non-hydrolyzable substituent, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon compounds only having hydrolyzable substituents and silicon compounds having a non-hydrolyzable substituent, with an aqueous alkali, in the presence of silanol groups, the aluminum concentration being maintained at less than 0.3 mol/l, the Al/Si molar ratio being maintained between 1 and 3.6 and the alkali/Al molar ratio being maintained between 2.3 and 3;

(b) stirring the mixture resulting from step (a) at ambient temperature in the presence of silanol groups long enough to form the hybrid aluminosilicate polymer; and

(c) eliminating the byproducts formed during steps (a) and (b)
5 from the reaction medium.

The expression "non-hydrolyzable substituent" means a substituent that does not separate from the silicon atom during the process and in particular at the time of treatment with the aqueous alkali. Such substituents are for example hydrogen, fluoride or an organic group. On the contrary the expression
10 "hydrolyzable substituent" means a substituent eliminated by hydrolysis in the same conditions. The expression "modified mixed aluminum and silicon alkoxide" means a mixed aluminum and silicon alkoxide in which the aluminum atom only has hydrolyzable substituents and the silicon atom has both hydrolyzable substituents and a non-hydrolyzable substituent. Similarly, the
15 expression "modified mixed aluminum and silicon precursor" means a precursor obtained by hydrolysis of a mixture of aluminum compounds and silicon compounds only having hydrolyzable substituents and silicon compounds having a non-hydrolyzable substituent. This is the non-hydrolyzable substituent that will be found again in the hybrid aluminosilicate polymer material of the present
20 invention. More generally, an "unmodified" compound is a compound that only consists of hydrolyzable substituents and a "modified" compound is a compound that consists of a non-hydrolyzable substituent. This material is characterized by a Raman spectrum similar to the material obtained in the previous synthesis, as well as bands corresponding to the silicon non-hydrolyzable substituent (bands linked
25 to the non-hydrolyzable substituent can be juxtaposed with other bands), the Raman spectrum being produced for the material resulting from step (b) and before step (c).

Dye mordants are preferably added to at least the base layer, optionally also the inner layer and/or the overcoat, in order to improve smear
30 resistance at high relative humidity. Any polymeric or non-polymeric, organic or

inorganic mordant can be used in the hydrophilic absorbing layer or layers of the invention provided it does not adversely affect light fade resistance unduly.

The term "mordant" means a compound which, when present in a composition, interacts with a dye to prevent diffusion through the composition.

5 The dye mordants employed in the present inkjet recording elements can be any material which is substantive to inkjet dyes. Examples of such mordants include cationic lattices such as disclosed in U.S. Pat. No. 6,297,296 and references cited therein, cationic polymers such as disclosed in U.S. Pat. No. 5,342,688, and multivalent ions as disclosed in U.S. Pat. No. 5,916, 673, the disclosures of which
10 are hereby incorporated by reference. A list of mordant and non-mordant monomers that may be used in polymeric mordants in the present invention are listed US20040142122 A1 published 20040722 to Taguchi et al., hereby incorporated by reference in its entirety.

It is also possible to employ an inorganic mordant as a mordant
15 according to the invention, including a polyvalent water-soluble metal salt or a hydrophobic metal salt compound, also disclosed in the above-cited US20040142122 A1. Typically, the inorganic mordant may, for example, be a salt or complex of a metal selected from the group consisting of magnesium, aluminum, calcium, scandium, titanium, vanadium, manganese, iron, nickel,
20 copper, zinc, gallium, germanium, strontium, yttrium, zirconium, molybdenum, indium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium, hafnium, tungsten and bismuth.

Alternately, other mordanting materials well known in the art may
25 be selected, such as inorganic particulates with high points of zero charge that may be selected such that their surfaces are positively charged under most conditions. A common example of such a mineral mordant is boehmite.

Suitable mordants also include cationic or neutral, inorganic metal ion containing colloids, and polymer bound metal ion containing colloids. Non-
30 limiting examples of polymer bound metal ion containing colloids include

aluminum salts of organic polymers such as hydroxypropyl methylcellulose crosslinked with aluminum ions as described in U.S. Pat. No. 5,686,602.

Preferably, a cationic polymer is used as a dye mordant, e.g., a polymeric quaternary ammonium compound, such as poly(dimethylaminoethyl)-methacrylate, polyalkylenepolyamines, and products of the condensation thereof with dicyanodiamide, amine-epichlorohydrin polycondensates, lecithin and phospholipid compounds. Examples of mordants useful in the invention include vinylbenzyl trimethyl ammonium chloride/ethylene glycol dimethacrylate, vinylbenzyl trimethyl ammonium chloride/divinyl benzene, poly(diallyl dimethyl ammonium chloride), poly(2-N,N,N-trimethylammonium)ethyl methacrylate methosulfate, poly(3-N,N,N-trimethyl-ammonium)propyl methacrylate chloride, a copolymer of vinylpyrrolidinone and vinyl(N-methylimidazolium chloride, and hydroxyethyl cellulose derivitized with (3-N,N,N-trimethylammonium)propyl chloride.

Some specific examples of water insoluble, cationic, polymeric particles which may be used in the invention include those described in U.S. Patent No. 3,958,995, hereby incorporated by reference in its entirety. Specific examples of these polymers include, for example, a terpolymer of styrene, (vinylbenzyl)dimethylbenzylamine and divinylbenzene (49.5:49.5:1.0 molar ratio); and a terpolymer of butyl acrylate, 2-aminoethylmethacrylate hydrochloride and hydroxyethylmethacrylate (50:20:30 molar ratio).

A cationic polymer, which comprises an effective amount of a cationic monomeric unit (mordant moiety), can be water-soluble or can be in the form of a latex, water dispersible polymer, beads, or core/shell particles wherein the core is organic or inorganic and the shell in either case is a cationic polymer. Such particles can be products of addition or condensation polymerization, or a combination of both. They can be linear, branched, hyper-branched, grafted, random, blocked, or can have other polymer microstructures well known to those in the art. They also can be partially crosslinked. Examples of core/shell particles useful in the invention are disclosed in U.S. Patent No. 6,619,797 issued

September 16, 2003 to Lawrence et al., titled "Inkjet Printing Method." Examples of water-dispersible particles useful in the invention are disclosed in U.S. Patent No. 6,454,404 issued September 24, 2002 to Lawrence et al., titled "Inkjet Printing Method," and U.S. Patent No. 6,503,608 issued January 7, 2003 to
5 Lawrence et al., titled "Inkjet Printing Method."

Preferably, cationic, polymeric particles comprising at least 10 mole percent of a cationic mordant moiety (monomeric unit) are employed in the base layer.

Such cationic, polymeric particles useful in the invention can be
10 derived from nonionic and cationic monomers. In a preferred embodiment, combinations of nonionic and cationic monomers are employed. The nonionic or cationic monomers employed can include neutral or cationic derivatives of addition polymerizable monomers such as styrenes, alpha-alkylstyrenes, acrylate esters derived from alcohols or phenols, methacrylate esters (usually referred to as
15 methacrylate), vinylimidazoles, vinylpyridines, vinylpyrrolidinones, acrylamides, methacrylamides, vinyl esters derived from straight chain and branched acids (e.g., vinyl acetate), vinyl ethers (e.g., vinyl methyl ether), vinyl nitriles, vinyl ketones, halogen-containing monomers such as vinyl chloride, and olefins, such as butadiene.

20 The nonionic or cationic monomers can also include neutral or cationic derivatives of condensation polymerizable monomers such as those used to prepare polyesters, polyethers, polycarbonates, polyureas and polyurethanes.

The water insoluble, cationic, polymeric particles that can optionally be employed as mordants in this invention can be prepared using
25 conventional polymerization techniques including, but not limited to bulk, solution, emulsion, or suspension polymerization. They are also commercially available usually from a variety of sources.

Mordants are preferably used, especially in the base layer, in an amount that is high enough that the images printed on the recording element will
30 have a sufficiently high smear resistance. In a preferred embodiment of the invention, cationic, polymeric particles are used in the amount of about 5 to 30

weight percent solids, preferably 10 to 20 weight percent in the base layer. If present, an optional additional hydrophilic absorbing layers below the inner layer may contain an amount of mordant particles in the same range.

The base layer preferably comprises a base-layer polymeric
5 mordant comprising between 1 and 10 percent solids of weakly mordanting cationic polymer comprising less than 50 mole percent of a cationic monomer, wherein substantially no other polymeric mordant is present in the base layer. Preferably, the base layer comprises between 2 and 8 percent by weight solids of the base-layer polymeric mordant.

10 In one embodiment, the base-layer comprises a polymeric mordant that is a non-particulate cationic polymer as a result of being coated in soluble form, and comprises between 10 to 30 mole percent of a cationic monomer that comprises free amines substantially protonated with an acid. Such a polymeric mordant may be a cationic polymer that is insoluble when in the unprotonated
15 form. In a particularly preferred embodiment, the base-layer polymeric mordant is a cationic acrylic polymer.

In one embodiment, a preferred cationic polymer for the base layer is a cationic acrylic polymer such as, for example, Glascol®R-350 (Ciba), which is an acrylic latex that can optionally be used in its solubilized form by lowering
20 the pH sufficiently. A preferred cationic acrylic polymer comprises alkyl methacrylate such as methyl or ethyl (meth)acrylate and dialkylaminoalkyl (meth)acrylates such as 2-trimethylammonium ethyl acrylate and/or methacrylate. Cationic acrylic polymers are also disclosed in EP 0216 479 B2 to Farrar (Allied Colloids Limited).

25 The support for the inkjet recording element used in the invention can be any of those usually used for inkjet receivers, such as resin-coated paper, paper, polyesters, or microporous materials such as polyethylene polymer-containing material sold by PPG Industries, Inc., Pittsburgh, Pennsylvania under the trade name of Teslin®, Tyvek® synthetic paper (DuPont Corp.), and
30 OPPalyte® films (Mobil Chemical Co.) and other composite films listed in U.S. Patent No. 5,244,861. Opaque supports include plain paper, coated paper,

synthetic paper, photographic paper support, melt-extrusion-coated paper, and laminated paper, such as biaxially oriented support laminates. Biaxially oriented support laminates are described in U.S. Patent Nos. 5,853,965; 5,866,282; 5,874,205; 5,888,643; 5,888,681; 5,888,683; and 5,888,714. These biaxially oriented supports include a paper base and a biaxially oriented polyolefin sheet, typically polypropylene, laminated to one or both sides of the paper base. Transparent supports include glass, cellulose derivatives, e.g., a cellulose ester, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate; polyesters, such as poly(ethylene terephthalate), poly(ethylene naphthalate), poly(1,4-cyclohexanedimethylene terephthalate), poly(butylene terephthalate), and copolymers thereof; polyimides; polyamides; polycarbonates; polystyrene; polyolefins, such as polyethylene or polypropylene; polysulfones; polyacrylates; polyetherimides; and mixtures thereof. The papers listed above include a broad range of papers, from high end papers, such as photographic paper to low end papers, such as newsprint. In a preferred embodiment, polyethylene-coated or poly(ethylene terephthalate) paper is employed.

The support used in the invention may have a thickness of from 50 to 500 μm , preferably from 75 to 300 μm . Antioxidants, antistatic agents, plasticizers and other known additives may be incorporated into the support, if desired.

In order to improve the adhesion of the base layer, or alternatively an optional additional lower base layer to the support, the surface of the support may be subjected to a corona-discharge treatment prior to applying a subsequent layer. The adhesion of the ink recording layers to the support may also be improved by coating a subbing layer on the support. Examples of materials useful in a subbing layer include halogenated phenols and partially hydrolyzed vinyl chloride-co-vinyl acetate polymer

Coating compositions employed in the invention may be applied by any number of well known techniques, including dip-coating, wound-wire rod coating, doctor blade coating, gravure and reverse-roll coating, slide coating, bead coating, extrusion coating, curtain coating and the like. Known coating and drying

methods are described in further detail in Research Disclosure no. 308119, published Dec. 1989, pages 1007 to 1008. Slide coating is preferred, in which the base layers and overcoat may be simultaneously applied. After coating, the layers are generally dried by simple evaporation, which may be accelerated by known
5 techniques such as convection heating.

To improve colorant fade, UV absorbers, radical quenchers or antioxidants may also be added to any one or more of the hydrophilic absorbing layers as is well known in the art. Other additives include pH modifiers, adhesion promoters, rheology modifiers, surfactants, biocides, lubricants, dyes, optical
10 brighteners, matte agents, antistatic agents, etc. In order to obtain adequate coatability, additives known to those familiar with such art such as surfactants, defoamers, alcohol and the like may be used. A common level for coating aids is 0.01 to 0.30 % active coating aid based on the total solution weight. These coating aids can be nonionic, anionic, cationic or amphoteric. Specific examples
15 are described in MCCUTCHEON's Volume 1: Emulsifiers and Detergents, 1995, North American Edition.

Matte particles may be added to any or all of the layers described in order to provide enhanced printer transport, resistance to ink offset, or to change the appearance of the ink receiving layer to satin or matte finish. In addition,
20 surfactants, defoamers, or other coatability-enhancing materials may be added as required by the coating technique chosen.

In another embodiment of the invention, a filled layer containing light scattering particles such as titania may be situated between a clear support material and the ink receptive multilayer described herein. Such a combination
25 may be effectively used as a backlit material for signage applications. Yet another embodiment which yields an ink receiver with appropriate properties for backlit display applications results from selection of a partially voided or filled poly(ethylene terephthalate) film as a support material, in which the voids or fillers in the support material supply sufficient light scattering to diffuse light
30 sources situated behind the image.

Optionally, an additional backing layer or coating may be applied to the backside of a support (i.e., the side of the support opposite the side on which the image-recording layers are coated) for the purposes of improving the machine-handling properties and curl of the recording element, controlling the friction and resistivity thereof, and the like.

Typically, the backing layer may comprise a binder and a filler. Typical fillers include amorphous and crystalline silicas, poly(methyl methacrylate), hollow sphere polystyrene beads, micro-crystalline cellulose, zinc oxide, talc, and the like. The filler loaded in the backing layer is generally less than 5 percent by weight of the binder component and the average particle size of the filler material is in the range of 5 to 30 μm . Typical binders used in the backing layer are polymers such as polyacrylates, gelatin, polymethacrylates, polystyrenes, polyacrylamides, vinyl chloride-vinyl acetate copolymers, poly(vinyl alcohol), cellulose derivatives, and the like. Additionally, an antistatic agent also can be included in the backing layer to prevent static hindrance of the recording element. Particularly suitable antistatic agents are compounds such as dodecylbenzenesulfonate sodium salt, octylsulfonate potassium salt, oligostyrenesulfonate sodium salt, laurylsulfosuccinate sodium salt, and the like. The antistatic agent may be added to the binder composition in an amount of 0.1 to 15 percent by weight, based on the weight of the binder. An image-recording layer may also be coated on the backside, if desired.

While not necessary, the hydrophilic material layers described above may also include a cross-linker. Such an additive can improve the adhesion of the ink receptive layer to the substrate as well as contribute to the cohesive strength and water resistance of the layer. Cross-linkers such as carbodiimides, polyfunctional aziridines, melamine formaldehydes, isocyanates, epoxides, and the like may be used. If a cross-linker is added, care must be taken that excessive amounts are not used as this will decrease the swellability of the layer, reducing the drying rate of the printed areas.

The coating composition can be coated either from water or organic solvents, however water is preferred. The total solids content should be selected

to yield a useful coating thickness in the most economical way, and for particulate coating formulations, solids contents from 10-40% are typical.

Inkjet inks used to image the recording elements of the present invention are well-known in the art. The ink compositions used in inkjet printing typically are liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, and the like. The solvent or carrier liquid can be solely water or can be water mixed with other water-miscible solvents such as polyhydric alcohols. Inks in which organic materials such as polyhydric alcohols are the predominant carrier or solvent liquid may also be used. Particularly useful are mixed solvents of water and polyhydric alcohols. The dyes used in such compositions are typically water-soluble direct or acid type dyes. Such liquid compositions have been described extensively in the prior art including, for example, U.S. Patent Nos. 4,381,946; 4,239,543; and 4,781,758.

The following example is provided to illustrate the invention.

Preparation 1

This example illustrates the preparation of an aluminosilicate that can be employed in the present invention. Osmosed water in the amount of 100 l was poured into a plastic (polypropylene) reactor. Then, 4.53 moles $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and then 2.52 moles tetraethyl orthosilicate were added. This mixture was stirred and circulated simultaneously through a bed formed of 1 kg of glass beads, 2-mm diameter, using a pump with 8-l/min output. The operation to prepare the unmodified mixed aluminum and silicon precursor took 90 minutes. Then, 10.5 moles NaOH 3M were added to the contents of the reactor in two hours. Aluminum concentration was 4.4×10^{-2} mol/l, Al/Si molar ratio 1.8 and alkali/Al ratio 2.31. The reaction medium clouded. The mixture was stirred for 48 hours. The medium became clear. The circulation was stopped in the glass bead bed. The aluminosilicate polymer material according to the present invention was thus obtained in dispersion form. Finally, nanofiltration was performed to pre-concentration by a factor of 3, followed by diafiltration using a Filmtec® NF 2540 nanofiltration membrane (surface area 6 m²) to eliminate the sodium salts to

obtain an Al/Na ratio greater than 100. The retentate resulting from the diafiltration by nanofiltration was concentrated to obtain a gel with about 20% by weight of aluminosilicate polymer.

Preparation 2

5 Another example of the preparation of aluminosilicate particles was as follows. Demineralized water in the amount of 56 kg was poured into a glass reactor. Then, 29 moles $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, were dissolved in the water and the reactor was heated to 40°C. Then, 19.3 moles tetraethyl orthosilicate were added. This mixture was stirred for 15 minutes. Next, 74.1 moles of triethylamine were
10 metered into the mixture in 75 minutes. The mixture was allowed to stir overnight. The mixture was diafiltered with a 20K MWCO spiral wound polysulfone membrane (Osmonics® model S8J) until the conductivity of the permeate was less than 1000 $\mu\text{S}/\text{cm}$. The reaction mixture was then concentrated by ultrafiltration. The yield was 41.3 kg at 6.14% solids (95%).

Preparation 3

15 This example illustrates the preparation of a solution for an Overcoat. A liquid solution was made by dissolving a partially hydrolyzed polyvinyl alcohol (KH-20® from Nippon Gohsei) in water and adding aluminosilicate particles such as prepared above, ethylenediamine tetracetic acid
20 (EDTA), and two coating surfactants (Olin 10G® from Olin Corp. and Zonyl FS300® from Dupont Corp.) with the ratios of dry chemicals being 91 parts KH-20® poly(vinyl alcohol) to 4.8 parts of the aluminosilicate and 1.9 parts Olin 10G® surfactant, 1.9 parts Zonyl FSN® surfactant, and 0.4 parts EDTA. The solution is made at 6% solids in water.

Preparation 4

25 This example illustrates the preparation of a solution for a Control Inner Layer 1 for Control Recording Element 1 below. A liquid solution was made by dissolving a partially hydrolyzed polyvinyl alcohol (Elvanol 52-22® DuPont) and adding a cationic polyurethane dispersion (Witcobond 213® from
30 Crompton Corp.) with the weight ratios of the dry chemicals being 77 parts

Elvanol 52-22® to 23 parts Witcobond 213® polyurethane. The solution is made at 5% solids in water.

Preparation 5

This example illustrates the preparation of a solution for a base layer. A liquid solution was made by dissolving a pigskin gelatin (commercially available from Nitta Gelatine Company) and adding a cationic mordant (Glascol R-350® commercially available from Ciba) that has been pH adjusted to 4.7 with acetic acid and adding 12 µm polystyrene polymer beads with the ratios of dry chemicals being 90 parts pigskin gelatin to 10 parts Glascol R-350® polymer to 0.6 parts 12 µm beads. The solution is made at 10% solids in water.

EXAMPLE 1

Control Recording Element 1 – Control element 1 is created by simultaneously coating the layers on a corona discharge treated polyethylene resin coated paper using a slide hopper and dried thoroughly by forced air heat after application of the coating solutions. The solution for the Base Layer is coated directly on the paper with the coating of the solution for the Control Inner Layer 1 on top of the Base Layer and the solution for Overcoat coated on top of Control Inner Layer 1 to yield dry thicknesses of 10.7 µm for the Base Layer, 1.65 µm for the Control Inner Layer 1, and 1.00 µm for the Overcoat Layer.

Control Recording Element 2 – This element was prepared exactly the same as for the Control Recording Element 1 except that 5 parts of aluminosilicate particles (such as prepared above) was added to the inner layer.

Control Recording Element 3 – This element was prepared exactly the same as for the Control Recording Element 1 except that 7.5 parts of aluminosilicate particles was added to the inner layer.

Control Recording Element 4 – This element was prepared exactly the same as for the Control Recording Element 1 except that the inner layer consisted of Elvanol 52-22® PVA only.

Control Recording Element 5 – This element was prepared exactly the same as for the Control Recording Element 4 except that 5 parts aluminosilicate particles was added to the inner layer.

Control Recording Element 6 – This element was prepared exactly the same as for the Control Recording Element 4 except that 10 parts aluminosilicate particles was added to the inner layer.

Control Recording Element 7 – This element was prepared exactly the same as for the Control Recording Element 4 except that 15 parts aluminosilicate particles was added to the inner layer.

Control Recording Element 8 – This element was prepared exactly the same as for the Control Recording Element 4 except that 20 parts aluminosilicate particles was added to the inner layer.

Invention Recording Element 1 – This element was prepared exactly the same as for the Control Recording Element 4 except that Elvanol 52-22® PVA was replaced with an acetoacetylated PVA (Z-320 Nippon Gohsei)

Invention Recording Element 2 – This element was prepared exactly the same as for the Invention Recording Element 1 except that 5 parts aluminosilicate particles was added to the inner layer.

Invention Recording Element 3 – This element was prepared exactly the same as for the Invention Recording Element 2 except that 10 parts aluminosilicate particles was added to the inner layer.

Invention Recording Element 4 – This element was prepared exactly the same as for the Invention Recording Element 2 except that 15 parts aluminosilicate particles was added to the inner layer.

Control Recording Element 9 – This element was prepared exactly the same as for the Invention Recording Element 2 except that 20 parts aluminosilicate particles was added to the inner layer.

Invention Recording Element 5 – This element was prepared exactly the same as for the Control Recording Element 4 except that Elvanol 52-22® PVA was replaced with a carboxylated PVA (T-340 Nippon Gohsei).

Testing:

A test image (group portrait) was printed with an Epson 960® desktop inkjet printer using the following printer settings: Media Type: Premium Glossy Photo Paper; Mode: Automatic.

- 5 After the image was allowed to dry for about 30 minutes, the image was rubbed vigorously with a paper tissue. The adhesion of the coated layer was then noted. If a coated layer was removed, the sample was given a “fail” rating. If the coating could not be removed the sample was given a “pass” rating. Also, the gloss of each element was analyzed at a 20° angle (gloss meter : BYK Gardner
- 10 Micro-TRI-glossmeter).

TABLE 1

Element No.	Inner Layer Constituents and Weight Ratio	Adhesion Result	20 Degree Dmin Gloss Result
Control Recording Element 1	PVA + Polyurethane 77 to 23	Fail	53.7
Control Recording Element 2	(PVA + Polyurethane) + Aluminosilicate 95(77-23) to 5	Fail	56.2
Control Recording Element 3	(PVA + Polyurethane) + Aluminosilicate 92.5(77-23) to 7.5	Fail	51.4
Control Recording Element 4	PVA	Fail	57.1
Control Recording Element 5	PVA + Aluminosilicate 95 to 5	Fail	53.7
Control Recording Element 6	PVA + Aluminosilicate 90 to 10	Fail	56.2
Control Recording Element 7	PVA + Aluminosilicate 85 to 15	Fail	56.0
Control Recording Element 8	PVA + Aluminosilicate 80 to 20	Pass	26.0
Invention Recording Element 1	Acetoacetylated PVA	Pass	56.4
Invention Recording Element 2	Acetoacetylated PVA + Aluminosilicate 95 to 5	Pass	57.3
Invention Recording Element 3	Acetoacetylated PVA + Aluminosilicate 90 to 10	Pass	56.5
Invention Recording Element 4	Acetoacetylated PVA + Aluminosilicate 85 to 15	Pass	52.3
Control Recording Element 9	Acetoacetylated PVA + Aluminosilicate 80 to 20	Pass	20.2
Invention Recording Element 5	Carboxylated PVA	Pass	49.7

The above results show that the use of acetoacetylated poly(vinyl alcohol) provides improved adhesion compared to poly(vinyl alcohol). The results show that the for the control elements, the coating adhesion is unacceptable except for Control Element 8 which comprised relatively high amounts of

5 aluminosilicate. However, the improvement in adhesion was obtained at the expense of a decrease in gloss, wherein the invention elements exhibited high gloss (preferably above 30, more preferably above 45) with acceptable adhesion.

CLAIMS:

1. An inkjet recording element comprising, in order over a support, at least three non-porous hydrophilic absorbing layers as follows:

- 5 (a) a base layer comprising as binder a hydrophilic synthetic or natural polymer;
- (b) an inner layer comprising acetoacetylated poly(vinyl alcohol) and/or carboxylated poly(vinyl alcohol) and optionally up to 15 weight % of particles of a synthetic, substantially amorphous aluminosilicate material; and
- 10 (c) an overcoat comprising poly(vinyl alcohol) binder and particles of a synthetic, substantially amorphous aluminosilicate material.

2. The inkjet recording element of claim 1, wherein the base layer comprises a polymeric or non-polymeric, organic or inorganic, mordant.

15

3. The inkjet recording element of claim 1, wherein the inner layer comprises acetoacetylated poly(vinyl alcohol) having a modification degree, in mol percent, of from 2.5 to 15 percent.

20

4. The inkjet recording element of claim 1, wherein the base layer comprises gelatin.

5. The inkjet recording element of claim 1, wherein the particles in the overcoat have an average diameter of 1 to 10 nm for the particles.

25

6. The inkjet recording element of claim 4, wherein the synthetic, substantially amorphous aluminosilicate material exhibits an X-ray diffraction pattern that comprises weak peaks at about 2.2 and 3.3 Å.

30

7. The inkjet recording element of claim 1, wherein there is an absence of a cationic or anionic polymeric mordant in the inner layer.

8. The inkjet recording element of claim 1 wherein the synthetic, substantially amorphous aluminosilicate material is substantially in the form of hollow spheres.

5 9. The inkjet recording element of claim 1 wherein the synthetic, substantially amorphous aluminosilicate material is a synthetic allophane with essentially no iron atoms.

10 10. The inkjet recording element of claim 1 wherein the synthetic, substantially amorphous aluminosilicate material is a synthetic allophane having a positive charge.

11. The inkjet recording element of claim 1 wherein the synthetic, substantially amorphous particles comprise a polymeric aluminosilicate having the
15 formula:



where the ratio of x:y is between 0.5 and 4, a and b are selected such that the rule of charge neutrality is obeyed; and n is between 0 and 10.

20 12. The inkjet recording element of claim 11 wherein the polymeric aluminosilicate comprises organic groups.

13. The inkjet recording element of claim 12 wherein the polymeric aluminosilicate has the formula:



where the ratio of x:y is between 1 and 3.6, and a and b are selected such that the rule of charge neutrality is obeyed; and n is between 0 and 10.

14. The inkjet recording element of claim 1 wherein the average
30 particle size of the synthetic, substantially amorphous material is in the range from about 3 nm to about 6 nm.

15. The inkjet recording element of claim 1 wherein the synthetic, substantially amorphous material is present in an amount of 5 to 30 weight percent solids.

5 16. The inkjet recording element of claim 11 wherein the synthetic, substantially amorphous aluminosilicate material is present in the ink-receiving inner layer in an amount of 5 to 30 weight percent solids and comprise substantially spherical hollow spheres, wherein the material is represented by the formula:



where the ratio of x:y is between 1 and 3.6, and a and b are selected such that the rule of charge neutrality is obeyed; and n is between 0 and 10.

17. The inkjet recording element of claim 1 wherein the
15 acetoacetylated poly(vinyl alcohol) has a degree of saponification of 80 to 100%.

18. The recording element of claim 1 wherein the acetoacetylated poly(vinyl alcohol) has a molecular weight of 15,000 to 150,000.

20 19. The recording element of claim 1 wherein the inkjet recording
element exhibits a 20 Degree Dmin Gloss of at least 35.

20. An inkjet printing method, comprising the steps of:

25 A) providing an inkjet printer that is responsive to digital data signals;

B) loading the inkjet printer with the inkjet recording element of Claim 1;

C) loading the inkjet printer with an inkjet ink; and

30 D) printing on the inkjet recording element using the inkjet
ink in response to the digital data signals.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/028370

A. CLASSIFICATION OF SUBJECT MATTER

B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 048 479 A (OJI PAPER CO., LTD) 2 November 2000 (2000-11-02) paragraphs '0040!', '0049!', '0053!', '0054!', '0066!; claim 1 -----	1-20
A	US 5 320 897 A (KONDO ET AL) 14 June 1994 (1994-06-14) column 8, line 5 - line 8 column 8, line 53 - line 55 -----	1-20
A	PATENT ABSTRACTS OF JAPAN vol. 007, no. 165 (M-230), 20 July 1983 (1983-07-20) & JP 58 072495 A (JIYUUJIYOU SEISHI KK), 30 April 1983 (1983-04-30) abstract ----- -/--	1-20



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/028370

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2005/072973 A (EASTMAN KODAK COMPANY; KAPUSNIAK, RICHARD JULIUS; ROMANO, CHARLES EUGE) 11 August 2005 (2005-08-11) page 7; claims 1-12 page 9	1-20
P,X	US 2005/158486 A1 (KAPUSNIAK RICHARD J ET AL) 21 July 2005 (2005-07-21) paragraphs '0027!, '0031!	1-20
E	WO 2005/072972 A (EASTMAN KODAK COMPANY; KAPUSNIAK, RICHARD JULIUS; ROMANO, CHARLES EUGE) 11 August 2005 (2005-08-11) the whole document	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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