

SPIRO COMPOUNDS AND METHODS FOR THE MODULATION OF
CHEMOKINE RECEPTOR ACTIVITY

This application claims benefit of U.S. Provisional
5 Application Serial No. 60/501,407, filed September 10,
2003, the entire disclosure of which is hereby
incorporated by reference.

TECHNICAL FIELD

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The present invention relates to novel spiro compounds
and a method of modulating chemokine receptor activity
using these compounds. The present invention is also
directed to novel spiro compounds which are useful in the
15 prevention or treatment of diseases associated with the
modulation of CCR5 chemokine receptor activity. The
present invention is further directed to a method of
blocking cellular entry of HIV in a subject and to
compositions using these compounds.

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BACKGROUND ART

Chemokines are chemotactic cytokines that are released by
a wide variety of cells to attract macrophages, T cells,
25 eosinophils, basophils and neutrophils to sites of
inflammation and they also play a role in the maturation
of cells of the immune system. Chemokines play an
important role in immune and inflammatory responses in
various diseases and disorders, including asthma,
30 rhinitis and allergic diseases, as well as autoimmune

- 1 -

WATER RESISTANT INK JET PRINTABLE SHEETBACKGROUND OF THE INVENTION

[0001] The present invention is directed to an ink jet recordable substrate. In particular, the present invention relates to a substantially water-resistant, at least partially coated, ink jet recordable substrate. The present invention is further directed to a multilayer article comprising the ink jet recordable substrate at least partially connected to a substantially nonporous material. Moreover, the present invention is directed to a process for producing the multilayer article. This application claims priority to 10/654,377 filed on September 3, 2003; 10/654,119 filed on September 3, 2003; and 10/654,433 filed on September 3, 2003.

[0002] It is known in the art to size paper with various sizing components for the purpose of retarding or preventing penetration of liquids into the structure. For example, "internal sizing" consists of introducing sizing materials into the pulp during the paper making operation. The sizing materials are precipitated onto the fibers primarily for the purpose of controlling penetration of liquids into the final dry paper. Further, "surface sizing" involves the application of dispersions of film-forming substances such as converted starches, gums, and modified polymers, to previously formed paper. Surface sizing imparts strength to the paper.

[0003] The use of sized paper to print with an ink jet printer containing predominantly water-based inks may yield imaged papers which have a tendency to curl into tubes. The use of un-sized paper may result migration of the image through the sheet and interference with the image on the other side, if one side of the imaged sheet comes into contact with water.

[0004] Various attempts have been made in the art to overcome the forgoing problems. For example, United States Patent 5,709,976 discloses a paper substrate coated with a

- 2 -

hydrophobic barrier material and an image-receiving layer. United States Patent 6,140,412 teaches a process for coating paper with an aqueous cationic polyurethane resin solution. Japanese Patent (JP) 11216945 discloses a process for coating paper with a composition that includes polyvinylpyrrolidone, a polyurethane resin emulsion, polyvinyl alcohol and a cationic resin. Further, United States Patent 6,020,058 discloses an acrylic composition and United States Patent 6,025,068 discloses a urethane-acrylic co-polymer.

[0005] United States Patents 4,861,644 and 5,196,262 disclose a microporous material sheet which includes a matrix of linear ultrahigh molecular weight polyolefin, a large proportion of finely divided water-insoluble siliceous filler, and interconnecting pores. U.S. Patent No. 6,025,068 teaches a method of coating a microporous polyolefin substrate with a coating composition which includes a binder dissolved or dispersed in a volatile aqueous liquid medium.

[0006] Another coating composition for ink jet recording materials is disclosed in Japanese Patent (JP) 2001-184881. This reference discloses a coating composition that includes a nonionic or anionic polyurethane and the reaction product of a monomeric secondary amine and epichlorohydrin. Japanese Patents (JP) 11268406 and (JP) 2000153667 disclose cationic polyurethanes useful in waterproofing coatings for ink jet printing substrates.

[0007] There remains a need for an ink jet recording medium that is durable, water-resistant and able to record sharp images when an ink jet printing ink is applied thereto.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a substantially water-resistant coating composition for an ink jet recordable substrate. The coating composition has a pH of less than 7 and includes:

(a) an aqueous polyurethane dispersion; and

- 3 -

(b) an aqueous solution of a nitrogen-containing polymeric dye fixative compound.

[0009] In a non-limiting embodiment, the coating composition of the present invention can further include an acrylic polymer.

[0010] The present invention is also directed to a method of at least partially coating an ink jet recordable substrate in which the above-described coating composition is applied to the substrate.

[0011] The present invention is further directed to an ink jet recordable substrate wherein at least one side of the substrate has at least a partial coating layer of the above-described coating composition.

[0012] The present invention is also directed to a multilayer article comprising a microporous substrate at least partially connected to a substantially nonporous material, said microporous substrate at least partially coated with the above-described coating composition.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Unless otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about."

[0014] Unless otherwise indicated, all references to (meth)acrylic, (meth)acrylate and (meth)acrylamide monomers is meant to include both the methacrylic and acrylic species.

[0015] Various numerical ranges are disclosed in this patent application. Because these ranges are continuous, they include every value between the minimum and maximum values. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations.

[0016] The coating composition of the present invention includes an aqueous polyurethane dispersion and an aqueous

- 4 -

solution of a nitrogen-containing polymeric dye fixative compound.

[0017] Suitable polyurethanes for use in the present invention can include any polyurethane that is substantially dispersible in water. Non-limiting examples of aqueous polyurethane dispersions for use in the present invention can include any known water-dispersible nonionic polyurethanes, anionic polyurethanes, cationic polyurethanes, and mixtures thereof.

[0018] The mixing of an anionic polymer and a cationic polymer can result in a polysalt which is often insoluble in water and other solvents. In the present invention, it has been found that the addition of an aqueous solution of a cationic nitrogen-containing polymer to an aqueous anionic polyurethane dispersion results in a stable dispersion which is useful as a coating composition for an ink jet recordable substrate. However, a reversal in the order of addition such that the anionic polyurethane dispersion is added to the aqueous solution of a cationic nitrogen-containing polymer, can result in the formation and precipitation of a polysalt from the aqueous solution.

[0019] In a non-limiting embodiment of the present invention, an aqueous dispersion of polyurethane resin comprising particles of a polyurethane polymer dispersed in an aqueous medium can be used in the present invention.

[0020] The polyurethane for use in the present invention can be prepared by a variety of methods known in the art. For example, a polyisocyanate can be reacted with a polyol to form a prepolymer, such as an isocyanate-terminated prepolymer. As used herein and the claims, the term "polyisocyanate" refers to a compound with more than one isocyanate group, such as but not limited to a diisocyanate. Non-limiting examples of suitable diisocyanates for use in the present invention include can include but are not limited to toluene diisocyanate, hexamethylene diisocyanate, isophorone

- 5 -

diisocyanate and dicyclohexyl methane diisocyanate. Non-limiting examples of suitable three or more functional isocyanates can include but are not limited to the reaction products of diisocyanates with polyols such as trimethylol propane, glycerol and pentaerythritol. In a non-limiting embodiment, the polyisocyanate for use in the present invention can include Desmodur which is commercially available from Bayer Corporation.

[0021] As used herein and in the claims, the term "polyol" refers to a compound with more than one hydroxyl group. Non-limiting examples of suitable polyols for use in the present invention can include polyols such as but not limited to those from which the polyisocyanate can be prepared, polyester polyols and polyether polyols.

[0022] The reaction of the polyisocyanate and polyol can be carried out in the presence of an organic solvent. Suitable organic solvents can include but are not limited to n-methyl pyrrolidone, tetrahydrofuran and glycol ether.

[0023] In a non-limiting embodiment, the prepolymer can be reacted with a di-hydroxyl compound having an acid group, such as dimethylol propionic acid, to produce a polyurethane with at least one pendant acid group. The acid group can include a carboxylic acid group or a sulfonic acid group. The polyurethane having a pendant acid group can then be reacted with a base to produce an anionic polyurethane.

[0024] An aqueous dispersion of an anionic polyurethane resin for use in the invention can include particles of an anionic polyurethane polymer dispersed in an aqueous medium. The polyurethane polymer can have at least one pendent acid group which may be neutralized in the presence of a base to form anionic group(s), which can stabilize the dispersion. The base can be selected from the group consisting of an inorganic base, ammonia, amine and mixtures thereof.

[0025] The anionic polyurethane for use in the invention can be prepared by methods known in the art. In a non-

- 6 -

limiting embodiment, (i) a polyisocyanate, (ii) a polyol, (iii) a compound having an acid group, and optionally (iv) a chain-extending compound such as a polyamine or hydrazine, can be reacted to produce an anionic polyurethane.

[0026] In a non-limiting embodiment, the isocyanate-terminated prepolymer can be dispersed in water in the presence of a base, and then chain extended by adding the polyamine. In a further non-limiting embodiment, the prepolymer is chain extended in an organic solvent solution and then the polyurethane polymer is dispersed in water in the presence of the base.

[0027] Suitable anionic polyurethanes for use in the present invention can include anionic polyurethanes based on aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, and/or aliphatic polycaprolactam polyurethanes. In a non-limiting embodiment, an anionic polyurethane dispersion for use in the present invention can be commercially obtained from Crompton Corporation under the trade name WitcoBond®.

[0028] In alternate non-limiting embodiments, the aqueous anionic polyurethane dispersion of the present invention can contain up to 70 wt.%, or up to 65 wt.%, or up to 60 wt.%, or up to 50 wt.% of the anionic polyurethane. In further alternate non-limiting embodiments, the aqueous anionic polyurethane dispersion includes at least 1 wt.%, or at least 5 wt.%, or at least 10 wt.%, or at least 20 wt.% of the anionic polyurethane. The amount of anionic polyurethane in the aqueous anionic polyurethane dispersion is not critical. In general, the amount should not be so much as to cause the dispersion itself or the mixture with the nitrogen-containing polymer to be unstable, or so little that the coating composition cannot provide sufficient water and rub resistance, or causes the dispersion itself to be unstable.

- 7 -

The anionic polyurethane can be present in the aqueous anionic polyurethane dispersion in any range of values inclusive of those stated above.

[0029] The cationic polyurethane dispersion for use in the present invention can include a wide variety of known water-dispersible cationic polyurethanes. Non-limiting examples can include but are not limited to those cationic polyurethanes which are commercially available from Crompton Corporation under the trade name Witcobond, such as, Witcobond W-213 and W-215 formulations.

[0030] The cationic polyurethane can be prepared by various methods known in the art. United States Patent 3,470,310 discloses the preparation of a water dispersion of polyurethane which contains salt-type groups bonded into the polyurethane. United States Patent 3,873,484 discloses an aqueous dispersion of polyurethane prepared from quaternized polyurethane prepolymer prepared by reacting alkoxylated diol, N-alkyl dialkanolamine, organic diisocyanate and quaternizing with dialkyl sulfate quaternizing agent. United States Patent 6,221,954 teaches a method for making polyurethane prepolymer in which N-monoalkanol tertiary amine is reacted with alkylene oxide in the presence of a strong acid to form a polyol salt, which is further reacted with an excess amount of organic polyisocyanate and chain extended with an active hydrogen-containing compound.

[0031] In alternate non-limiting embodiments, the aqueous cationic polyurethane dispersion for use in the present invention can contain up to 70 wt.%, or up to 65 wt.%, or up to 60 wt.%, or up to 50 wt.% of the cationic polyurethane. In further alternate non-limiting embodiments, the aqueous cationic polyurethane dispersion can include at least 1 wt.%, or at least 5 wt.%, or at least 10 wt.%, or at least 20 wt.% of the cationic polyurethane. The amount of cationic polyurethane in the aqueous cationic polyurethane dispersion is not critical. In general, the amount should not be so much

- 8 -

as to cause the dispersion itself or the mixture with the nitrogen-containing polymer to be unstable, or so little that the coating composition does not provide sufficient water and rub resistance, or cause the dispersion itself to be unstable. The cationic polyurethane can be present in the aqueous cationic polyurethane dispersion in any range of values inclusive of those stated above.

[0032] The nonionic polyurethane dispersion for use in the present invention can be selected from a variety of known water-dispersible nonionic polyurethanes. The nonionic polyurethane can be prepared by various methods known in the art. For example, Szycher (i.e., "Szycher's Book of Polyurethanes" by Michael Szycher, CRC Press, New York, NY, 1999, pages 14-10 through 14-15) describes the preparation of water dispersions of polyurethanes, which contain hydrophilic polyether-type groups either branching off or terminating on the main polyurethane chains. Polyethylene oxide units (having a molecular weight (MW) of from 200 to 4,000) can be used as dispersing sites. In alternate non-limiting embodiments, nonionic polyurethanes can be prepared using diols or diisocyanate comonomers bearing pendant polyethylene oxide chains.

[0033] In alternate non-limiting embodiments, the aqueous nonionic polyurethane dispersion for use in the present invention can contain up to 70 wt.%, or up to 65 wt.%, or up to 60 wt.%, or up to 50 wt.% of the nonionic polyurethane. In further alternate non-limiting embodiments, the aqueous nonionic polyurethane dispersion can include at least 1 wt.%, or at least 5 wt.%, or at least 10 wt.%, or at least 20 wt.% of the nonionic polyurethane. The amount of nonionic polyurethane present in the aqueous nonionic polyurethane dispersion is not critical. In general, the amount should not be so much as to cause the dispersion itself or the mixture with the nitrogen-containing polymer to be unstable, or so little that the coating composition does not provide

- 9 -

sufficient water and rub resistance, or cause the dispersion itself to be unstable. The nonionic polyurethane can be present in the aqueous nonionic polyurethane dispersion in any range of values inclusive of those stated above.

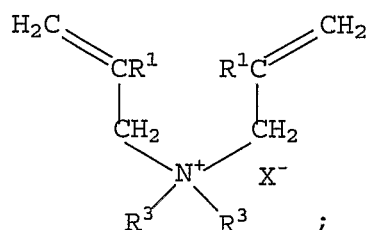
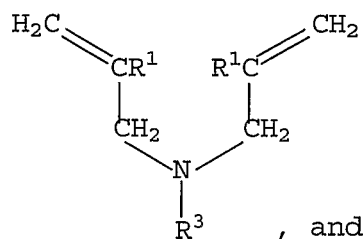
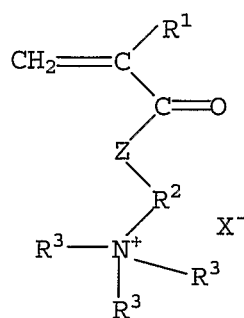
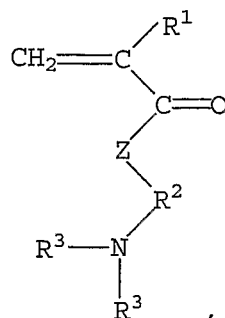
[0034] In alternate non-limiting embodiments of the present invention, the aqueous solution of a nitrogen-containing polymer for use as a dye fixative in the coating composition, can have a pH of less than 7, or less than 6, or less than 5. A pH value within this range allows for at least a portion of the nitrogen atoms to carry at least a portion of a charge. In further alternate non-limiting embodiments, the resulting coating composition can have a pH of less than 7, or less than 6, or less than 5. Further, on selected substrates the wetting action of the coating composition can be improved when the pH is within the aforementioned ranges. In a non-limiting embodiment, a coating composition for use in commercial applications can have pH greater than 2.

[0035] As used herein and in the claims, "aqueous solution" means that the nitrogen-containing polymer is at least partially soluble in a liquid medium such as water.

[0036] A dye fixative is generally used to fix dyes to a substrate to preclude the dyes from bleeding or migrating out of the substrate when the substrate is contacted with water.

[0037] A known cationic nitrogen-containing polymer in which at least a portion of the nitrogen atoms carry at least a portion of a cationic charge within the above-mentioned pH range of the coating composition, can be used in the present invention as a dye fixative. Suitable cationic nitrogen-containing polymers can include cationic polymers having one or more monomer residues derived from one or more of the following nitrogen-containing monomers:

- 10 -



wherein R^1 represents independently for each occurrence in each structure, H or C_1 to C_3 aliphatic; R^2 represents independently for each structure a divalent linking group selected from C_2 to C_{20} aliphatic hydrocarbon, polyethylene glycol and polypropylene glycol; R^3 represents independently for each occurrence in each structure H, C_1 to C_{22} aliphatic hydrocarbon or a residue from the reaction of the nitrogen with epichlorohydrin; Z is selected from $-\text{O}-$ or $-\text{NR}^4-$, where R^4 is H or CH_3 ; and X is a halide or methylsulfate.

- 11 -

[0038] Non-limiting examples of nitrogen-containing monomers or resulting monomer residues for use in the present invention can include dimethyl aminoethyl (meth)acrylate, (meth)acryloyloxyethyl trimethyl ammonium halides, (meth)acryloyloxyethyl trimethyl ammonium methylsulfate, dimethyl aminopropyl (meth)acrylamide, (meth)acrylamidopropyl trimethyl ammonium halides, aminoalkyl (meth)acrylamides where the amine is reacted with epichlorohydrin, (meth)acrylamidopropyl trimethyl ammonium methylsulfate, diallyl amine, methyl diallyl amine, and diallyl dimethyl ammonium halides.

[0039] In a non-limiting embodiment, the nitrogen-containing polymers can contain additional monomer residues. The additional monomer residues can be obtained from a variety of polymerizable ethylenically unsaturated monomer that, when copolymerized with the nitrogen-containing monomers, allows the resulting polymer to be at least partially soluble in water. As used herein and the claims, "partially soluble" refers to at least 0.1 gram of the polymer dissolving in water when ten (10) grams of the polymer is added to one (1) liter of water and mixed for a period of 24 hours.

[0040] Non-limiting examples of monomers that can be copolymerized with the nitrogen-containing monomers include (meth)acrylamide, n-alkyl (meth)acrylamides, (meth)acrylic acid, alkyl esters of (meth)acrylate, glycol esters of (meth)acrylic acid, polyethylene glycol esters of (meth)acrylic acid, hydroxyalkyl (meth)acrylates, itaconic acid, alkyl ethers of itaconic acid, maleic acid, mono- and di-alkyl esters of maleic acid, maleic anhydride, maleimide, aconitic acid, alkyl esters of aconitic acid, allyl alcohol and alkyl ethers of allyl alcohol.

[0041] In alternate non-limiting embodiments, the nitrogen-containing polymer can be a homopolymer of a nitrogen-containing monomer, or a copolymer of one or more nitrogen-containing monomers. In another embodiment, the nitrogen-

- 12 -

containing polymer can be a copolymer of one or more polymerizable ethylenically unsaturated monomers and one or more nitrogen-containing monomers. When the nitrogen-containing polymer includes any of the aforementioned additional polymerizable ethylenically unsaturated comonomers, the nitrogen-containing polymer can include not more than 70 mol%, or not more than 50 mol%, or not more than 25 mol%, or not more than 10 mol% of the nitrogen-containing monomer. The amount of nitrogen-containing monomer can depend on the polyurethane used in the present coating composition. In general, when the amount of the nitrogen-containing monomer used in the nitrogen-containing polymer is too much, an unstable mixture of the nitrogen-containing polymer and polyurethane dispersion can result. It can be difficult to properly apply an unstable mixture to an ink jet recordable substrate.

[0042] In alternate non-limiting embodiments, when the nitrogen-containing polymer includes any of the aforementioned additional polymerizable ethylenically unsaturated comonomers, the nitrogen-containing polymer can include at least 0.1 mol%, or at least 1.0 mol%, or at least 2.5 mol%, or at least 5.0 mol% of the nitrogen-containing monomer. In further alternate non-limiting embodiments, when the amount of nitrogen-containing monomer in the nitrogen-containing polymer is too little, the nitrogen-containing polymer cannot provide adequate dye fixative properties and a recorded ink image on the coated substrate can lack sufficient water and rub fastness properties.

[0043] The nitrogen-containing monomers can be present in the nitrogen-containing polymer in any range of values inclusive of those stated above. The additional polymerizable ethylenically unsaturated monomers can be present in an amount such that the total percentage is 100 mol%.

[0044] In alternate non-limiting embodiments of the present invention, the aqueous solution of the nitrogen-containing

- 13 -

polymeric dye fixative includes at least 5 wt.%, or at least 10 wt.%, or at least 15 wt.% of the nitrogen-containing polymer; and not more than 50 wt.%, or not more than 45 wt.%, or not more than 40 wt.% of the nitrogen-containing polymer. In general, when the concentration of the nitrogen-containing polymer is too little, it may not be economical for commercial applications and can be too dilute to provide optimum ratios with the polyurethane. In general, when the concentration is too much, the solution can be too viscous to easily handle in a commercial environment. Non-limiting examples of cationic nitrogen-containing polymers useful in the present invention can include solutions of polyamide amines reacted with epichlorohydrin, which are commercially available under the trade name CinFix from Stockhausen GmbH & Co. KG, Krefeld, Germany.

[0045] In alternate non-limiting embodiments, the ink jet recordable substrate coating composition of the present invention can include from 10 wt.% to 70 wt.%, or from 20 wt.% to 60 wt.%, or from 30 wt.% to 50 wt.% of an aqueous polyurethane dispersion; and from 30 wt.% to 90 wt.%, or from 40 wt.% to 80 wt.%, or from 50 wt.% to 70 wt.% of an aqueous solution of the nitrogen-containing polymer. The weight percentages are based on the total weight of the ink jet recordable substrate coating composition.

[0046] In a non-limiting embodiment of the present invention, the coating composition of the present invention can include an acrylic polymer. The acrylic polymer can be selected from a wide variety of anionic, cationic and nonionic acrylic polymers known to a person skilled in the art.

[0047] Non-limiting examples of suitable cationic acrylic polymers can include but are not limited to polyacrylates, polymethacrylates, polyacrylonitriles and polymers having monomer types selected from the group consisting of acrylonitrile, acrylic acid, acrylamide and mixtures thereof.

- 14 -

[0048] The cationic acrylic polymer can be prepared by a variety of methods known in the art. In a non-limiting embodiment, a cationic acrylic polymer can be synthesized via a free radical solution polymerization from monomer types butyl acrylate, methyl methacrylate and 2-(tert-butylamino)ethyl methoacrylate. The molar equivalent of butyl acrylate can be from 0.10 to 0.95, or from 0.15 to 0.75; the molar equivalent of methyl methacrylate can be from 0.10 to 0.85, or from 0.15 to 0.70; and the molar equivalent of 2-(tert-butylamino)ethyl methacrylate can be from 0.10 to 0.25, or from 0.12 to 0.20. The reaction mixture can be treated with acid such that the pH is within a range of from 4.0 to 7.0. The mixture then can be diluted with water and solvent stripped. Non-limiting examples of suitable acids for use in the treatment step can include a wide variety of acids which can function as a solubilizing or dispersing agent to produce a stable dispersion of a cationic polymer. Non-limiting examples of suitable solvents for use in the stripping process can include but are not limited to isopropanol and methyisobutyl ketone (MIBK).

[0049] In alternate non-limiting embodiments of the present invention, the molar equivalent of butyl acrylate, methyl methacrylate and 2-(tert-butylamino)ethyl methacrylate, can be from 0.200 to 0.250 : 0.600 to 0.630 : 0.150 to 0.170, respectively ; or from 2.19 to 0.621 to 0.160, respectively.

[0050] In further alternate non-limiting embodiments, the cationic acrylic polymer for use in the present invention can have a number average molecular weight of at least 1500 or less than 8000; or from 1500 to 8150, or from 2900 to 7125.

[0051] In alternate non-limiting embodiments of the present invention, the ink jet recordable substrate coating composition can include from 20 wt.% to 75 wt.%, or from 25 wt.% to 70 wt.%, or from 30 wt.% to 60 wt.% of aqueous polyurethane dispersion; from 5 wt.% to 75 wt.%, or from 15 wt.% to 70 wt.%, or from 30 wt.% to 65 wt.% of aqueous

- 15 -

solution of the nitrogen-containing polymer; and from 1 wt.% to 75 wt.%, or from 20 wt.% to 60 wt.%, or from 25 wt.% to 50 wt.% of acrylic polymer. The weight percentages are based on the total weight of the ink jet recordable substrate coating composition.

[0052] In another non-limiting embodiment of the present invention, water can be present with the nitrogen-containing polymer, polyurethane and acrylic polymer. When water is present, the resulting ink jet recordable substrate coating composition can have a total resin solids of from 5 wt.% to 35 wt.%, or from 5 wt.% to 20 wt.%, or from 5 wt.% to 15 wt.% based on the total weight of the ink jet recordable substrate coating composition. In general, a total resin solids that is too high, can cause the viscosity of the coating composition to increase such that the resulting penetration of the coating composition to the substrate can be less than desired. In general, a total resin solids that is too low, can cause the viscosity of the coating composition to decrease such that the resulting penetration of the coating to the substrate can be less than desired. In alternate non-limiting embodiments, the viscosity of the coating composition can be less than 500 cps, or less than 400 cps and at least 10 cps, or at least 25 cps when measured using a Brookfield viscometer at 25°C.

[0053] In a further non-limiting embodiment, the coating composition of the present invention can include a co-solvent. Suitable co-solvents can include a wide variety known to a person skilled in the art. Non-limiting examples can include but are not limited to lower alkyl alcohols, n-methylpyrrolidone, Dowanol PM, toluene, and glycol ethers.

[0054] The coating composition of the present invention can also include other additives typically known in the art. Such additives can include but are not limited to surfactants, such as nonionic, cationic, anionic, amphoteric and zwitterionic surfactants; rheology modifiers, such as polyvinyl alcohols, polyvinyl pyrrolidones, polyethylene oxides, polyacrylamides,

- 16 -

natural and synthetic gums; biocides, such as a blend of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazolin-3-one available commercially by the trade name Kathon, from Rohm and Haas Co., 2-hydroxypropylmethane thiosulfonate, and dithiocarbamates; and coupling agents, such as titanium, silane-type, trisodium pyrophosphate.

[0055] The present invention is also directed to a method of preparing the ink jet recordable substrate coating composition. In a non-limiting embodiment, the aqueous solution of a nitrogen-containing polymer can be added into an aqueous polyurethane dispersion. In another non-limiting embodiment, the acrylic polymer can be added. Sufficient mixing can be maintained during the addition such that a homogeneous mixture can result.

[0056] The present invention is further directed to a method of coating an ink jet recordable substrate. The method includes the steps of:

- (a) providing an ink jet recordable substrate having a top surface and a bottom surface;
- (b) providing the coating composition described above; and
- (c) applying the coating composition to at least one surface of the ink jet recordable substrate.

[0057] A variety of ink jet recordable substrate known in the art can be used in the present invention. In a non-limiting embodiment, the ink jet recordable substrate can include a cellulosic-based paper. United States Patents 4,861,644 and 5,196,262 describe suitable microporous substrates for use in the present invention.

[0058] In another non-limiting embodiment, the ink jet recordable substrate can be a microporous substrate. A non-limiting example of a suitable microporous substrate can include an ink jet recordable substrate having a top surface and a bottom and which includes:

- (a) a matrix comprising a polyolefin;

- 17 -

(b) a particulate siliceous filler distributed throughout the matrix; and

(c) a network of pores wherein the pores constitute at least 35 percent by volume of the microporous substrate.

[0059] A wide variety of polyolefins known in the art such as but not limited to polyethylene or polypropylene can be used in the microporous substrate. In a non-limiting embodiment, the polyethylene can be a linear high molecular weight polyethylene having an intrinsic viscosity of at least 10 deciliters/gram and the polypropylene can be a linear high molecular weight polypropylene having an intrinsic viscosity of at least 5 deciliters/gram. As used herein and the claims, "high molecular weight" refers to a weight average molecular weight of from 20,000 to 2,000,000.

[0060] Intrinsic viscosity can be determined using a variety of conventional techniques. As recorded herein and in the claims, intrinsic viscosity is determined by extrapolating to zero concentration the reduced viscosities or the inherent viscosities of several dilute solutions of the polyolefin wherein the solvent is distilled decahydronaphthalene to which 0.2 percent by weight, 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid, neopentametetracyl ester [CAS Registry No. 6683-19-8] has been added. The reduced viscosities or the inherent viscosities of the polyolefin are ascertained from relative viscosities obtained at 135°C using an Ubbelohde No. 1 viscometer.

[0061] On a coating-free, printing ink free, impregnant-free, and pre-bonding basis, pores constitute at least 35 percent by volume of the microporous substrate. In alternate non-limiting embodiments, the pores can constitute at least 60 percent by volume of the microporous substrate, or from 35 percent to about 80 percent, or from 60 percent to 75 percent by volume of the microporous substrate.

- 18 -

[0062] In alternate non-limiting embodiments, the siliceous particles can be in the form of ultimate particles, aggregates of ultimate particles, or a combination of both. As used herein and in the claims, the term "ultimate particles" refers to small discrete particles of colloidal polymerized silicic acid units which make up amorphous silica. The term "aggregate" as used herein and in the claims, refers to a structure wherein ultimate particles are condensed to produce an open but essentially continuous structure of chains or a solid structure of substantially interconnecting pores.

[0063] In an embodiment, the siliceous particles are finely-divided. As used herein and in the claims, "finely-divided" refers to a maximum retention of 0.01% by weight on a 40-mesh sieve screen.

[0064] In a further non-limiting embodiment, the siliceous particles can be substantially insoluble. As used herein and in the claims, the term "substantially insoluble" refers to amorphous silica exhibiting a reproducible equilibrium solubility in water which can range from 70 ppm to greater than 150 ppm in water at a temperature of 25°C. It is believed that variations in solubility can be due to differences in particle size, state of internal hydration and the presence of trace impurities in the silica or absorbed on its surface. The solubility of the silica can also depend on the pH of the water. As pH increases from neutrality (i.e., pH of 7) to alkalinity (i.e., pH greater than 9), the solubility of silica can also increase. (See "The Chemistry of Silica", R.K. Iler, Wiley-Interscience, NY (1979), pp. 40-58.)

[0065] In a non-limiting embodiment of the present invention, at least 90 percent by weight of the siliceous particles used in preparing the microporous substrate can have particle sizes in the range of from 5 to 40 micrometers. The particle size can be determined by a variety of conventional techniques. In present invention, a Model TaII Coulter Multisizer Particle Size Analyzer (Coulter Electronics, Inc.)

- 19 -

was use, wherein prior to analysis by the Coulter Analyzer, the filler was stirred for 10 minutes in Isoton II electrolyte solution (Curtin Matheson Scientific, Inc.) using a four-blade, 4.445 centimeter diameter propeller stirrer. In a non-limiting embodiment, at least 90 percent by weight of the siliceous particles can have particle sizes in the range of from 10 to 30 micrometers. It is believed that the sizes of filler agglomerates can be reduced during processing of the ingredients to prepare the microporous substrate.

[0066] Suitable siliceous particles can include a wide variety known to a person skilled in the art. Non-limiting examples can include but are not limited to particles of silica, mica, montmorillonite, kaolinite, asbestos, talc, diatomaceous earth, vermiculite, natural and synthetic zeolites, cement, calcium silicate, aluminum silicate, sodium aluminum silicate, aluminum polysilicate, alumina silica gels, and glass particles. In a non-limiting embodiment, silica and clay can be used as siliceous particles. In a further non-limiting embodiment, precipitated silica, silica gel, or fumed silica can be used.

[0067] In general, silica can be prepared by combining an aqueous solution of a soluble metal silicate with an acid. The soluble metal silicate can be an alkali metal silicate such as sodium or potassium silicate. The acid can be selected from the group consisting of mineral acids, organic acids, and carbon dioxide. The silicate/acid slurry can then be aged. An acid or base can be added to the silicate/acid slurry. The resultant silica particles can be separated from the liquid portion of the mixture; the separated silica can be washed with water; the wet silica product can be dried; and the dried silica can be separated from residues of other reaction products; using conventional washing, drying and separating methods.

[0068] In a non-limiting embodiment, the siliceous particles can be coated using the above-described coating

- 20 -

compositions prior to incorporation into the microporous substrate. A variety of methods known in the art can be used to at least partially coat the particles. The selected coating method is not critical. In a further non-limiting embodiment, the coating ingredients can be added to an aqueous slurry of pre-washed silica filter cake under sufficient stirring to allow for substantially complete mixing of the ingredients, followed by drying, using conventional techniques known in the art.

[0069] United States Patent Applications having serial numbers 09/636,711; 09/636,312; 09/636,310; 09/636,308; 09/636,311 and 10/041,114; disclose suitable coating compositions and methods of coating silica particles which may be used in the present invention.

[0070] In alternate non-limiting embodiments, the particulate siliceous filler can constitute from 50% to 90%, or from 55% to 85%, or from 60% to 80% by weight of the microporous substrate.

[0071] In a non-limiting embodiment, in addition to the siliceous particles, substantially water-insoluble non-siliceous filler particles can also be used in the microporous substrate. Non-limiting examples of such optional non-siliceous filler particles can include but are not limited to particles of titanium oxide, iron oxide, copper oxide, zinc oxide, antimony oxide, zirconia, magnesia, alumina, molybdenum disulfide, zinc sulfide, barium sulfate, strontium sulfate, calcium carbonate, magnesium carbonate, magnesium hydroxide, and finely divided substantially water-insoluble flame retardant filler particles such as but not limited to particles of ethylenebis(tetra-bromophthalimide), octabromodiphenyl oxide, decabromodiphenyl oxide, and ethylenebisdibromonorbornane dicarboximide.

[0072] In a non-limiting embodiment of the invention, the substrate can be highly porous. The term "highly porous" refers to a substrate having a porosity of not more than

- 21 -

20,000, or not more than 10,000 or not more than 7,500 seconds/100cc air. In a further non-limiting embodiment, the porosity can be at least 50 seconds/100cc air. These porosity values are determined in accordance with the method described in ASTM D726, with the following exceptions relative to Section 8 of the ASTM method. In the present invention, the sheet samples are tested without conditioning in accordance with ASTM D685, and only three (3) specimens for a given sample type are tested for a total of six (6) measurements (three measurements per two surfaces) for a given specimen type rather than a minimum of ten specimens for a given sample as stated in ASTM D726. In general, the lower the value in seconds/cc air, the more porous is the substrate. Highly porous substrates can be produced by various methods known in the art, such as thermally treating a substrate, orienting, compositionally by increasing the filler content, microvoiding films, or etching. Non-limiting examples of highly porous substrates can include but are not limited to thermally-treated microporous substrates such as Teslin® TS-1000 which is commercially available from PPG Industries, Inc., Pittsburgh, PA.

[0073] In alternate non-limiting embodiments of the present invention, the coated microporous substrate can have a thickness of at least 0.1 mils, or from 0.5 to 100 mils, or from 1 to 50 mils, or from 4 to 14 mils. In general, when the coated microporous substrate has a thickness which exceeds the aforementioned ranges, it may not feed properly through an ink jet printer. In general, when the thickness of the coated microporous substrate is less than the stated ranges, it may not have sufficient strength for its intended use.

[0074] A wide variety of methods known in the art can be used to at least partially apply the coating composition of the present invention to the ink jet recordable substrate. Non-limiting examples of suitable methods can include but are not limited to flexography, spraying, air knife coating,

- 22 -

curtain coating, dipping, rod coating, blade coating, gravure, reverse roll, roller application, imbibing, size press, printing, brushing, drawing, slot-die coating, and extrusion.

[0075] In a non-limiting embodiment of the present invention, the coating composition can be at least partially applied to the substrate using an air knife coating technique where at least a portion of the excess coating can be 'blown off' by a powerful jet from the air knife. In another non-limiting embodiment, a reverse roll coating method can be used. In this procedure, the coating composition can be measured onto an applicator roller by precision setting of the gap between an upper metering roller and the application roller below it. The coating can be at least partially wiped-off the application roller by the substrate as it passes around the support roller at the bottom.

[0076] In another non-limiting embodiment of the present invention, gravure coating can be used to at least partially apply the coating composition. In the gravure coating method, an engraved roller runs in a coating bath, which at least partially fills the engraved dots or lines of the roller with the coating composition. At least a portion of the excess coating on the roller can be at least partially wiped-off by a doctor blade and the coating can be deposited onto the substrate as it passes between the engraved roller and a pressure roller. Reverse gravure coating methods also can be used. In this method, the coating composition can be metered by the engraving on a roller before being at least partially wiped-off as in a conventional reverse roll coating process.

[0077] In a further non-limiting embodiment, a metering rod can be used to at least partially apply the coating composition. When a metering rod is used, at least a portion of the excess of the coating can be deposited onto the substrate as it passes over a bath roller. The wire-wound metering rod, sometimes known as a Meyer Bar, allows the desired quantity of the coating to remain on the substrate.

- 23 -

The quantity is determined by the diameter of the wire used on the rod.

[0078] The amount of the substantially dry coating applied to the substrate, or "coat weight", can be measured as coating weight per coated area. The coat weight can vary widely. In an alternate non-limiting embodiment, the coat weight can be at least 0.001 g/m^2 , or at least 0.01 g/m^2 , or at least 0.1 g/m^2 ; or not more than 50 g/m^2 , or not more than 40 g/m^2 , or not more than 35 g/m^2 . The coat weight can vary between any of the stated amounts.

[0079] Following application of the coating composition to the substrate, solvent can be removed from the applied coating by any conventional drying technique. In a non-limiting embodiment, the coating can be dried by exposing the coated substrate to a temperature ranging from ambient to 350°F .

[0080] The coating composition can be at least partially applied at least one time to at least one surface of the substrate. In a non-limiting embodiment, the coating composition can be applied more than one time. In this embodiment, the applied coating can be at least partially dried between coating applications.

[0081] When the coating composition is applied to a microporous substrate, the coating composition can at least partially penetrate into the substrate. Penetration of the coating into the microporous substrate can improve the ink jet print quality on the coated substrate. In alternate non-limiting embodiments, the coating can penetrate into at least the first one (1) micron, or at least the first ten (10) microns, or at least the first twenty (20) microns or at least the first thirty (30) microns of the microporous substrate.

[0082] The present invention is also directed to a coated microporous substrate. The coated microporous substrate can include at least one coated surface. The surface can be coated with the aforementioned coating compositions using the above-described coating techniques.

- 24 -

[0083] In alternate non-limiting embodiments, the substantially dried coating layer can include polyurethane in an amount of from 10 to 70 percent, or from 20 to 60 percent, or from 30 to 55 percent by weight of the coating layer; and nitrogen-containing polymer in an amount of from 30 to 90 percent, or from 40 to 80 percent, or from 45 to 70 percent by weight of the coating layer. The amount of each component in the substantially dried coating layer can be determined by the amount of each used to prepare the coating composition.

[0084] As used herein and in the claims, "substantially dry" is used to refer to the coating layer that feels dry to touch.

[0085] The ink jet recordable substrate can be printed with a wide variety of printing inks using a wide variety of printing processes. Both the printing inks and the printing processes are themselves conventional and known in the art. In a non-limiting embodiment, the substrate of the present invention can be used as an ink jet recordable substrate for ink jet printing. In alternate non-limiting embodiments, printing can be accomplished prior to assembly of the ink jet recordable substrate into multilayer articles of the present invention or following the assembly of such multilayer articles.

[0086] In the present invention, the substantially water-resistant, at least partially coated, ink jet recordable substrate can be connected to at least one substantially nonporous material. As used herein and the claims, the term "connected to" means to link together or place in relationship either directly, or indirectly by one or more intervening materials. As used herein and the claims, the term "substantially nonporous material" refers to a material which is generally impervious to the passage of liquid, gas, and bacteria. On a macroscopic scale, a substantially nonporous material exhibits few if any pores. As used herein and the claims, the term "pore(s)" refers to a minute opening(s)

- 25 -

through which matter can pass. Substantially nonporous materials for use in the present invention can vary widely and can comprise those materials customarily recognized and employed for their known barrier properties. Non-limiting examples of such suitable materials can include substantially nonporous thermoplastic polymers, substantially nonporous metalized thermoplastic polymers, substantially nonporous thermoset polymers, substantially nonporous elastomers, and substantially nonporous metals. The substantially nonporous material can be in the form of a sheet, film, or foil, or other shapes can be used when desired, such as for example, plates, bars, rods, tubes, and forms of more complex shape. In further alternate non-limiting embodiments, the substantially nonporous material for use in the present invention can be in the form of a sheet, film or foil.

[0087] As used herein and the claims, the term "thermoplastic polymer" refers to a polymer that can be softened by heat and then regain its original properties upon cooling. The term "thermoset polymer" as used herein and the claims refers to a polymer that solidifies or sets on heating and cannot be re-melted.

[0088] Non-limiting examples of suitable thermoplastic polymeric materials can include but are not limited to polyethylene, high density polyethylene, low density polyethylene, polypropylene, poly(vinyl chloride), saran, polystyrene, high impact polystyrene, nylons, polyesters such as poly(ethylene terephthalate), copolymers of ethylene and acrylic acid, copolymers of ethylene and methacrylic acid, and mixtures thereof. In further alternate non-limiting embodiments, all or a portion of the carboxyl groups of carboxyl-containing copolymers can be neutralized with sodium, zinc, or the like. A non-limiting example of a metalized thermoplastic polymeric material can be aluminized poly(ethylene terephthalate).

- 26 -

[0089] Non-limiting examples of suitable thermoset polymeric materials can include but are not limited to thermoset phenol-formaldehyde resin, thermoset melamine-formaldehyde resin, and mixtures thereof.

[0090] Non-limiting examples of suitable elastomeric materials can include but are not limited to natural rubber, neoprene, styrene-butadiene rubber, acrylonitrile-butadiene-styrene rubber, elastomeric polyurethanes, and elastomeric copolymers of ethylene and propylene.

[0091] Non-limiting examples of suitable metals can include but are not limited to iron, steel, copper, brass, bronze, chromium, zinc, die metal, aluminum, and cadmium.

[0092] The multilayer article of the present invention can be constructed using a wide variety of known methods for at least partially connecting at least one layer of an ink jet recordable substrate with at least one layer of a substantially nonporous material. In a non-limiting embodiment, at least one layer of a substantially water-resistant, at least partially coated ink jet recordable substrate can be fusion bonded to at least one layer of a substantially nonporous material. The ink jet recordable substrate generally comprises opposed major surfaces which are characteristic of sheets, films, foils, and plates. The resulting multilayer article can comprise one layer or more than one layer of the ink jet recordable substrate, and one layer or more than one layer of the substantially nonporous material. In a non-limiting embodiment, at least one exterior layer can be the ink jet recordable substrate. In an alternate non-limiting embodiment, the ink jet recordable substrate can be a microporous substrate.

[0093] In a non-limiting embodiment, the multilayer article of the present invention can be produced by fusion bonding in the absence of an adhesive. Fusion bonding can be accomplished using conventional techniques such as sealing through use of heated rollers, heated bars, heated plates,

- 27 -

heated bands, heated wires, flame bonding, radio frequency (RF) sealing, and ultrasonic sealing. Solvent bonding can be used where the substantially nonporous material can be at least partially soluble in the applied solvent to the extent that the surface becomes tacky. The ink jet recordable substrate can be contacted with the tacky surface, and the solvent then can be removed to form the fusion bond. In a non-limiting embodiment, foamable compositions can be foamed in at least partial contact with the ink jet recordable substrate to form a fusion bond between the foam and the substrate. Films or sheets of nonporous substrate can be extruded and while still hot and tacky, can be contacted with the ink jet recordable substrate to form a fusion bond. The fusion bond can be permanent or peelable, depending upon the known bonding technique and/or the nature of the substantially nonporous material employed.

[0094] In a non-limiting embodiment, heat sealing can be used to fusion bond the ink jet recordable substrate to the substantially nonporous material. In general, heat sealing can include inserting an ink jet recordable substrate into standard heat sealing equipment which is known in the art. In a non-limiting embodiment, the ink jet recordable substrate can be inserted in conjunction with a substantially nonporous material which can be a thermoplastic and/or thermoset polymer. Heat and/or pressure can be applied to the substrate/polymer construction for a period of time. The amount of heat and/or pressure and length of time can vary widely. In general, the temperature, pressure and time are selected such that the substrate and polymer can be at least partially connected together to form a multilayer article. In a non-limiting embodiment, the temperature can be within the range of from 100°F to 400°F. In another non-limiting embodiment, the pressure can be within the range of from 5 psi to 250 psi. In a further non-limiting embodiment, the time period can range from one (1) second to thirty (30) minutes.

- 28 -

The multilayer article then can be cooled while under pressure for a period of time, such as but not limited to thirty (30) minutes. Although the strength of the bond formed between the substrate and polymer can vary, the strength is generally such that it can exceed the tensile properties of the substrate alone.

[0095] In a non-limiting embodiment, the substantially nonporous material can be polyvinyl chloride.

[0096] In a non-limiting embodiment, the ink jet recordable substrate employed in the present invention can be at least partially connected to a nonporous substrate such as polyethylene and polypropylene by heat sealing in the absence of an extrinsic adhesive. The resultant fusion bond can be sufficiently strong which is surprising inasmuch as the lamination of materials to polyolefins is typically difficult unless special adhesives are used.

[0097] In alternate non-limiting embodiments, the ink jet recordable substrate can be substantially continuously at least partially connected to the substantially nonporous material, or it can be discontinuously at least partially connected to the substantially nonporous material. Non-limiting examples of discontinuous bonds can include bonding areas in the form of one or more spots, patches, strips, stripes, chevrons, undulating stripes, zigzag stripes, open-curved stripes, closed-curved stripes, irregular areas, and the like. In alternate non-limiting embodiments, when patterns of bonds are present, they can be random, repetitive, or a combination of both.

[0098] In another non-limiting embodiment, an ink jet recordable substrate can be at least partially connected to a substantially nonporous material in the presence of an adhesive. The adhesive for use in the present invention can be selected from a wide variety of adhesives known in the art. Suitable adhesives can include those having a sufficient molecular weight and viscosity such that the adhesive will not

- 29 -

substantially migrate into or substantially penetrate the ink jet recordable substrate. Migration or penetration of the adhesive into the substrate can reduce the tack and bond strength of the adhesive. Non-limiting examples of suitable adhesives for use in the present invention can include but are not limited to polyvinyl acetate, starches, gums, polyvinyl alcohol, animal glues, acrylics, epoxies, polyethylene-containing adhesives, and rubber-containing adhesives. In alternate non-limiting embodiments, the adhesive can be applied to the substrate, or to the substantially nonporous material, or to both the substrate and the substantially nonporous material. In a further non-limiting embodiment, the adhesive can be introduced via the use of a tie carrier coating.

[0099] The process of bonding the substrate and substantially nonporous material in the presence of an adhesive can be accomplished using a variety of conventional techniques known in the art. In a non-limiting embodiment, the substrate/adhesive/material construction can be inserted into standard processing equipment. Heat and/or pressure can be applied to the substrate/adhesive/material construction for a period of time. The amount of heat and/or pressure and length of time can vary widely. In general, the temperature, pressure and time are selected such that the substrate and substantially nonporous material can be at least partially connected together to form a multi-layer article. In a non-limiting embodiment, the temperature can be within the range of from 100°F to 400°F. In another non-limiting embodiment, the pressure can be within the range of from 5 psi to 250 psi. In still another non-limiting embodiment, the period of time can be in the range of from one (1) second to thirty (30) minutes. The multilayer article then can be cooled under pressure for a time period, such as thirty (30) minutes. Although the strength of the bond formed between the ink jet recordable substrate and the substantially nonporous material

- 30 -

can vary, the bond is generally such that it exceeds the tensile properties of the substrate alone.

[00100] The ink jet recordable substrate of the present invention can be molded using conventional molding techniques known in the art. In alternate non-limiting embodiments, the substrate can be molded in the presence of or in the absence of a substantially nonporous material, such as but not limited to a thermoplastic and/or thermoset polymer. In general, the ink jet recordable substrate can be inserted into standard molding equipment. In a non-limiting embodiment, a thermoplastic and/or thermoset polymer can be introduced onto the substrate and then the substrate/polymer construction can be inserted into the mold cavity. In another non-limiting embodiment, the substrate can be placed into the mold cavity and then the thermoplastic and/or thermoset polymer can be introduced onto the substrate. Heat and/or pressure can be applied to the substrate/polymer construction for a period of time. The amount of heat and/or pressure and length of time can vary widely. In general, the temperature, pressure and time can be selected such that the substrate and polymer can be at least partially connected together to form a multi-layer article. A typical temperature can be within the range of from 100°F to 400°F. In a non-limiting embodiment, wherein the polymer comprises a thermoplastic polymer, the substrate/polymer construction can be heated to a temperature that equals or exceeds the melt temperature of the thermoplastic polymer. In another non-limiting embodiment, wherein the thermoplastic polymer can be amorphous, the substrate polymer construction can be heated to a temperature that equals or exceeds the Vicat temperature. In still another non-limiting embodiment, wherein the polymer comprises a thermoset polymer, the temperature can be below the curing or crosslinking temperature of the polymer. A typical pressure can be within the range of from 5 psi to 250 psi, and a typical period of time can be in the range of from one (1)

- 31 -

second to fifteen (15) minutes. A typical result of a molding process can be a re-shaping of the original article. The re-shaping is generally defined by the design of the mold cavity. Thus, in a standard molding process, a two-dimensional flat sheet can be re-shaped into a three-dimensional article.

[00101] In a non-limiting embodiment of the present invention, the ink jet recordable substrate can comprise Teslin® which is commercially available from PPG Industries, Incorporated in Pittsburgh, PA. The thickness of the ink jet recordable substrate of the present invention can vary widely depending on the application or use. In a non-limiting embodiment, the ink jet recordable substrate can be from 5 to 20 mils thick.

[00102] In general, the multilayer article of the present invention can be produced employing a variety of molding and laminating procedures known in the art, which include but are not limited to compression molding, rotational molding, injection molding, calendering, roll/nip laminating, thermoforming, vacuum forming, extrusion coating, continuous belt laminating, and extrusion laminating.

[00103] In a non-limiting embodiment, other tie coatings known in the art can be used in conjunction with the substrate and the substantially nonporous material.

[00104] In another non-limiting embodiment, a friction-reducing coating composition can be at least partially applied to at least one of the ink jet recordable substrate and the substantially nonporous material. In a further non-limiting embodiment, the friction-reducing coating composition can comprise at least one lubricant and at least one resin. There are a wide variety of lubricants and resins known to the skilled artisan that can be used.

[00105] Non-limiting examples of such suitable lubricants can include but are not limited to natural and synthetic waxes, natural and synthetic oils, polypropylene waxes, polyethylene waxes, silicone oils and waxes, polyesters,

- 32 -

polysiloxanes, hydrocarbon waxes, carnauba waxes, microcrystalline waxes and fatty acids, and mixtures thereof. In a non-limiting embodiment, the lubricant for use in the present invention can include polysiloxanes, such as but not limited to silicone.

[00106] Non-limiting examples of suitable resins can include but are not limited to polyurethanes, polyesters, polyvinyl acetates, polyvinyl alcohols, epoxies, polyamides, polyamines, polyalkylenes, polypropylenes, polyethylenes, polyacrylics, polyacrylates, polyalkylene oxides, polyvinyl pyrrolidones, polyethers, polyketones, and co-polymers and mixtures thereof. In a non-limiting embodiment, the resin for use in the present invention can include styrene acrylic polymers such as but not limited to styrene acrylic-comprising polyurethanes, polyepoxies, polyvinyl alcohols, polyesters, polyethers, and co-polymers and mixtures thereof.

[00107] In a further non-limiting embodiment, the friction-reducing coating composition for use in the present invention can include Wikoff SCW 4890 and 2295 which are commercially available from Wikoff Industries, Incorporated, as poly board aqua coat products.

[00108] Not intending to be bound by any particular theory, it is believed that the molecules of the resin component of the friction-reducing coating can be at least partially interconnected or interlinked with the ink jet recordable substrate and/or the substantially nonporous material, such that the silicone can be essentially fixed to the surface of said substrate and/or said material. In a non-limiting embodiment, the molecules of a thermoplastic resin component can be at least partially interconnected by fusion to the ink jet recordable substrate and/or the substantially nonporous material. In another non-limiting embodiment, the molecules of a thermoset resin component can be at least partially interlinked by crosslinking to the ink jet recordable substrate and/or the substantially nonporous material.

- 33 -

[00109] In a further non-limiting embodiment, the friction-reducing coating composition can comprise water and/or an organic solvent. A wide variety of organic solvents known to the skilled artisan can be used. Non-limiting examples of such suitable organic solvents can include but are not limited to N-methyl pyrrolidone (NMP), methyl ethyl ketone (MEK), acetone, diethyl ether, toluene, Dowanol PM, Butyl Cellosolve, and mixtures thereof. In a non-limiting embodiment, the friction-reducing coating composition can comprise water and an organic solvent, wherein said organic solvent is at least partially miscible with water.

[00110] In a non-limiting embodiment, the friction-reducing coating composition can be at least partially applied to at least one of the ink jet recordable substrate and the substantially nonporous material of the present invention. Application of said friction-reducing coating composition to said substrate and/or said material can employ a wide variety of known techniques. In alternate non-limiting embodiments, the techniques described previously herein for applying the substantially water-resistant coating to the ink jet recordable substrate can be used for application of the friction-reducing coating composition to the ink jet recordable substrate and/or the substantially nonporous material.

[00111] The amount of the substantially dry friction-reducing coating applied to the substrate/material, or "coat weight", is typically measured as coating weight per coated area. The coat weight can vary widely. In alternate non-limiting embodiments, the coat weight of the substantially dry friction-reducing coating can be at least 0.1 gram per square meter, or from greater than 0 to 50 grams per square meter, or from 1 gram per square meter to 15 grams per square meter.

[00112] In a non-limiting embodiment, the multilayer article of the present invention can include a 10 mil thick sheet of Teslin® comprising a essentially water-resistant coating

- 34 -

composition, a 10 mil sheet of polyvinylchloride, a 10 mil thick sheet of polyvinylchloride, and a 2 mil thick sheet of polyvinylchloride comprising a friction-reducing coating composition. In a further non-limiting embodiment, the friction-reducing coating composition can comprise a polysiloxane and a styrene acrylic polymer.

[00113] In a non-limiting embodiment, the multilayer article of the present invention can include a magnetizable material. As used herein and the claims, the term "magnetizable material" means a material to which magnetic properties can be communicated. A wide variety of magnetizable materials are known to one skilled in the art. Known magnetizable materials are available in various forms such as but not limited to sheet, film, tape or stripe.

[00114] Magnetizable materials for use in the present invention can be selected from a variety of materials capable of being magnetized by a magnetic field. Suitable magnetizable materials can include but are not limited to oxide materials. Non-limiting examples of suitable oxide materials can include ferrous oxide, iron oxide, and mixtures thereof. In a non-limiting embodiment, the oxide particles can be present in a slurry formulation.

[00115] Suitable magnetizable materials for use in the present invention can include those known in the art which demonstrate performance characteristics such as but not limited to the ability to be encoded with sufficient ease, ability to encode a sufficient amount of information, and ability to be erased with sufficient resistance. In a non-limiting embodiment, the amount of information encoded onto the magnetizable material can be referred to as the number of stages or tracks. The number of stages or tracks can vary. In alternate non-limiting embodiments, the magnetizable material for use in the present invention can have at least one (1) track, or not more than six (6) tracks, or from three (3) to four (4) tracks.

- 35 -

[00116] In a non-limiting embodiment, the resistance to erasure can be referred to as "coercivity". In general, the higher the coercivity value, the greater the resistance to erasure. The coercivity value can vary. In alternate non-limiting embodiments, the magnetizable material for use in the present invention can have a coercivity of at least 200, or not more than 5000, or from 500 to 2500, or from 100 to 1500.

[00117] Non-limiting examples of suitable magnetizable materials for use in the present invention can include but are not limited to magnetic foils which are commercially available from JCP, Kurz, EMTEC and DuPont.

[00118] In a non-limiting embodiment, the magnetizable material can be at least partially connected to at least one or more materials selected from a protective material, a carrier material or an adhesive material. The protective material, carrier material and adhesive material can be selected from a wide variety of materials known in the art as useful for each function. Non-limiting examples of suitable protective materials can include but are not limited to PET (polyethylene terephthalate), polyester and combinations thereof. Non-limiting examples of carrier materials can include but are not limited to PET, polyester and combinations thereof. Non-limiting examples of suitable adhesive materials can include but are not limited to those recited herein.

[00119] In another non-limiting embodiment, the protective material can be at least partially connected to the magnetizable material, the magnetizable material can be at least partially connected to the carrier material, and the carrier material can be at least partially connected to the adhesive material.

[00120] In alternate non-limiting embodiments, the magnetizable material can be at least partially connected to an ink jet recordable substrate and/or at least one substantially nonporous material. Non-limiting examples of ink jet recordable substrates can include but are not limited

- 36 -

to those previously recited herein. In a non-limiting embodiment, the ink jet recordable substrate can be a microporous substrate such as those previously recited herein. In a further non-limiting embodiment, the microporous substrate can be Teslin® printing sheet which is commercially available from PPG Industries, Incorporated. Non-limiting examples of suitable substantially nonporous materials can include but are not limited to those previously recited herein. In a non-limiting embodiment, the substantially nonporous material can be polyvinyl chloride.

[00121] The magnetizable material-containing multilayer article of the present invention can be prepared by various methods known in the art. In a non-limiting embodiment, the magnetizable material can be at least partially connected to at least one substantially nonporous material. Various application techniques suitable for at least partially connecting the magnetizable material to the substantially nonporous material are known to a skilled artisan. In a non-limiting embodiment, the magnetizable material can be at least partially connected using an adhesive material. Non-limiting examples of suitable adhesive materials can include but are not limited to a wide variety of adhesives known to the skilled artisan, such as but not limited to those previously recited herein. In a non-limiting embodiment, the adhesive material can be selected from thermal- or pressure-sensitive adhesives.

[00122] In a further non-limiting embodiment, the magnetizable material can be at least partially connected to the adhesive material, and the adhesive material can be at least partially connected to a surface of the microporous substrate and/or at least one substantially nonporous material.

[00123] In alternate non-limiting embodiments, the magnetizable material can be at least partially connected to a microporous substrate and/or at least one substantially

- 37 -

nonporous material prior to, during, or following a conventional lamination process such as but not limited to the lamination process previously described herein.

[00124] In another non-limiting embodiment, the magnetizable material can be essentially flush with the surface of the microporous substrate and/or substantially nonporous material to which it can be connected.

[00125] In a non-limiting embodiment, a substantially water-resistant coating composition can be at least partially applied to the magnetizable material. In alternate non-limiting embodiments, the coating can be at least partially applied to the magnetizable material either prior to or following at least partially connecting the magnetizable material to a microporous substrate or a substantially nonporous material. In a further non-limiting embodiment, an adhesive material can be at least partially applied to the uncoated surface of the magnetizable material, and the adhesive-containing surface can be at least partially connected to the microporous substrate or substantially nonporous material. In alternate non-limiting embodiments, the substantially water-resistant coating composition can be at least partially applied to at least one of the magnetizable material, the microporous substrate and the substantially nonporous material. In still a further non-limiting embodiment, the substantially water-resistant coating composition can include that which is recited herein.

[00126] In a non-limiting embodiment, a friction reducing coating composition can be at least partially applied to the magnetizable material. In alternate non-limiting embodiments, the coating can be at least partially applied to the magnetizable material either prior to or following at least partially connecting the magnetizable material to a microporous substrate or a substantially nonporous material. In a further non-limiting embodiment, an adhesive material can be at least partially applied to the uncoated surface of the

- 38 -

magnetizable material, and the adhesive-containing surface can be at least partially connected to the microporous substrate or substantially nonporous material. In alternate non-limiting embodiments, the friction reducing coating composition can be at least partially applied to at least one of the magnetizable material, the microporous substrate, and substantially nonporous material. In still a further non-limiting embodiment, the substantially friction reducing coating composition can include that which is recited herein.

[00127] The coating compositions can be applied by a variety of methods known in the art. In alternate non-limiting embodiments, the coating compositions can be applied by the methods previously described herein.

[00128] In a further non-limiting embodiment, a multilayer article of the present invention can include a microporous substrate at least partially connected to a first substantially nonporous material; the first substantially nonporous material can be at least partially connected to a second substantially nonporous material; the second substantially nonporous material can be at least partially connected to a third substantially nonporous material; said third substantially nonporous material can include a magnetizable material. In a further non-limiting embodiment, the microporous substrate and/or substantially nonporous materials can be at least partially connected using an adhesive material which can be at least partially applied to at least one surface of the substrate and/or materials.

[00129] In another non-limiting embodiment, a release liner can be at least partially connected to at least one surface of the multilayer article of the present invention. The release liner can function as a barrier to essentially prevent or minimize damage of the article during the manufacture process. In a non-limiting embodiment, a coating residue can be deposited on the stainless steel equipment during the lamination process as a result of print-off. Deposition of

- 39 -

the coating on the equipment can result in at least partial damage to the coated surface of the multilayer article. In alternate non-limiting embodiments, a release liner can be at least partially connected to a coated or uncoated magnetizable material, a coated or uncoated substantially nonporous material, and/or a coated or uncoated microporous substrate.

[00130] The release liner can be selected from a wide variety of materials known in the art to perform the above-stated function. In general, a material suitable for use as a release liner in the present invention can have at least one of the following characteristics: a melt temperature in excess of the lamination temperature, the ability to essentially not migrate into the material and an acceptable tear strength such that it can be pulled away with sufficient ease.

[00131] In a further non-limiting embodiment, the microporous substrate, the substantially non-porous material, and magnetizable-containing substantially non-porous material can be aligned in an essentially parallel configuration to form a stacked article.

[00132] In another non-limiting embodiment, the microporous substrate can be at least partially connected to the substantially nonporous material in the absence of an adhesive material. In another non-limiting embodiment, the substantially nonporous material can be at least partially connected to another substantially nonporous material in the absence of an adhesive material.

[00133] In another non-limiting embodiment, the multilayer article of the present invention can include a data transmittance/storage device. Such devices can vary widely. Suitable devices for use in the present invention can include those known in the art. In a non-limiting embodiment, the device can include an antenna, electronic chip and/or other related circuitry. In a further embodiment, the device can include a carrier material. The carrier material can be

- 40 -

selected from a wide variety of materials known in the art. In a non-limiting embodiment, the carrier material can be a substantially nonporous material. Suitable substantially nonporous materials can include those previously recited herein. In a non-limiting embodiment, the carrier material can be polyvinylchloride.

[00134] In still a further embodiment, the device can include a barrier material on at least one side of the circuitry. A function of the barrier material can be to encompass the circuitry and provide a substantially flat surface on the outside of the device. The barrier material can be selected from a wide variety of materials known in the art. In a non-limiting embodiment, the barrier material can be a substantially nonporous material. Suitable substantially nonporous materials can include those previously recited herein. In a non-limiting embodiment, the barrier material can be polyvinylchloride.

[00135] In a non-limiting embodiment, the multilayer article of the present invention can include an ink jet recordable substrate, a data transmittance/storage device, and at least one substantially nonporous material. The ink jet recordable substrate can be selected from a wide variety of such materials known in the art. Suitable non-limiting examples can include those previously described herein. In a non-limiting embodiment, the ink jet recordable substrate can be a microporous substrate such as those previously recited herein. In a further non-limiting embodiment, the ink jet recordable substrate can be Teslin® printing sheet which is commercially available from PPG Industries, Incorporated. As previously described herein, the ink jet recordable substrate can be at least partially coated on at least one surface or uncoated. Suitable coating compositions can include those previously described herein. In a non-limiting embodiment, a substantially water-resistant coating composition can be at least partially applied to the ink jet recordable substrate.

- 41 -

[00136] The substantially nonporous material can be selected from a wide variety of such materials known in the art. Suitable non-limiting examples of substantially nonporous materials can include those previously described herein. In a non-limiting embodiment, the substantially nonporous material can be polyvinylchloride. As previously described herein, the substantially nonporous material can be at least partially coated on at least one surface or uncoated. Suitable coating compositions can include those previously described herein. In a non-limiting embodiment, a friction-reducing coating composition can be at least partially applied to the substantially nonporous material.

[00137] In a further non-limiting embodiment, the data transmittance/storage device can be at least partially connected to the barrier material using an adhesive material. A wide variety of suitable adhesive materials and methods of application are known in the art. Non-limiting examples include those adhesive materials and methods of application previously described herein.

[00138] In another non-limiting embodiment, the barrier material can have at least one surface at least partially coated with a coating composition. Suitable coating compositions can include those previously described herein. In a non-limiting embodiment, a friction-reducing coating composition can be at least partially applied to the barrier material.

[00139] In a non-limiting embodiment, the multilayer article with magnetizable material or with a transmittance/storage device, can have a thickness that varies widely. In alternate non-limiting embodiments, the thickness of the article can be at least 10 mils, or less than 60 mils, or from 30 to 50 mils.

[00140] The multilayer article with magnetizable material or with a data transmittance/storage device can be useful in a wide variety of applications. In alternate non-limiting embodiments, it can be used in applications related to

- 42 -

security access, access-control, data storage and data transmittance.

[00141] The multilayer article of the present invention has many and varied uses including but not limited to gaskets, cushion assemblies, signs, cards, printing substrates, substrates for pen and ink drawings, maps (particularly maritime maps), book covers, book pages, wall coverings, and seams, joints, and seals of breathable packages.

[00142] The multilayer article of the present invention can be useful for the purpose of decorating or identifying the substantially nonporous material, or imparting to the substantially nonporous material unique properties of the substrate surface. The ink jet recordable substrate can be decorated with a variety of methods including but not limited to: offset/lithographic printing, flexographic printing, painting, gravure printing, inkjet printing, electrophotographic printing, sublimation printing, thermal transfer printing, and screen printing. Decorating can also include at least partially applying a single or multilayer coating to the ink jet recordable substrate via normal coating methods known in the art. In general, the unique properties that an ink jet recordable substrate can impart on a substantially nonporous material include, but are not limited to one or more of: improved surface energy, increased porosity, decreased porosity, increased bond strength of post coat layer, and modification of the polymer's surface texture or pattern.

[00143] Polymer processing techniques are disclosed in U.S. Patent No. 4,892,779.

[00144] The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight and all references to water are meant to be deionized water.

EXAMPLESExample 1

[00145] A coating composition of the present invention was prepared by diluting in a stainless steel mix tank under high speed mixing with an overhead mixer, a 61.5% solids by weight anionic polyurethane dispersion sold under the trade name WitcoBond® 234 available from Crompton Corporation, Greenwich, Connecticut, to 9.22% solids by weight. In a separate feed tank a 55% solids by weight solution of a polyamide amine reacted with epichlorohydrin sold under the trade name CinFix NF by Stockhausen GmbH & Co. KG, Krefeld, Germany, was diluted to 5.78% solids by weight, and subsequently added to the diluted anionic polyurethane dispersion, and the mixture was mixed for 15 minutes. The pH was adjusted with glacial acetic acid to 5.0 ± 0.5 . The total resin solids of the mixture was 7.5% and the viscosity of the mixture was 46 cps as measured using a Brookfield viscometer, RVT, spindle no. 1, at 50 rpm and 25°C.

Examples 2-5

[00146] A coating composition was prepared as described in Example 1 and applied to Teslin® microporous substrates. Two substrates (Examples 2 and 4) were coated using a metering bar. A metering bar was placed 1 - 2 inches above the Teslin® sheet, parallel to the top edge. A 10 - 20 ml quantity of coating was drawn into a disposable plastic syringe. The coating was deposited as a bead strip (approximately 1/8 inches wide) directly next to and touching the metering bar. The bar was drawn completely across the sheet of Teslin®, attempting a continuous/constant rate. The resultant wet sheet was placed in a forced air oven, secured and dried at 95°C for 2 minutes. The dried sheet was removed from the oven and the same coating procedure was repeated on the opposite side of the sheet. The sheet was then printed and tested. For coating

- 44 -

compositions having a total resin solids of 7.5%, the viscosity was 46 cps; and for 10.0% solids, the viscosity was 63 cps. The viscosity values were measured using a Brookfield viscometer, RVT, spindle no. 1, at 50 rpm and 25°C.

[00147] Two substrates (Examples 3 and 5) were coated using a flexographic or gravure coating method to apply the coating. In this coating method, a line consisting of two coating stations, each with a forced air drying oven was used. Each coating station consists of a coating feed chamber, anilox roll and rubber application roll. The coating feed chamber was supplied from a coating holding tank and pump. Both sides of the Teslin® sheet were coated. The apparatus was fitted with a 7 BCM (billion cubic microns) anilox roll, line speed was 180 fpm, oven temperature was 105°C (220°F) and 8 passes per roll were made, which translates into four passes per surface.

[00148] The coating compositions were applied with an approximate coat weight of 0.73 g/m² (total front and back). The coat weight was determined as follows: the coat weight of "X" grams of coating (as dry solids) consumed in coating "Y" square meters of Teslin®, is "X divided by Y" grams per square meter.

[00149] Table 1 shows the characteristics of the sheets produced.

TABLE 1

	Substrate	Polyurethane	Coating Method	Total Resin Solids %
Example 2	Teslin® TS1000	WitcoBond 234	Meyer #9 Rod	7.5
Example 3	Teslin® TS1000	WitcoBond 234	7 BCM Anilox (5 BPS*)	7.5
Example	Teslin®	WitcoBond 234	Meyer #9 Rod	10.0

- 45 -

4	TS1000			
Example 5	Teslin® TS1000	WitcoBond 234	7 BCM Anilox (4 BPS*)	10.0

*BPS = Bumps Per Surface

[00150] The resultant coated sheets were printed with a test print pattern on a Model HP970 (Hewlett Packard Company) ink jet printer. Color bars from the test print pattern were measured for optical density by submerging in deionized water at ambient temperature for a period of 15 minutes, removing from the water and allowing to air dry for one hour and measuring each color for optical density. The optical density of cyan(C), magenta (M), yellow, black (K) and composite black (CMY) were measured using a Model RD922, MacBeth ANSWER II densitometer, manufactured by Kolimorgen Instrument Corporation, before and after water soak. The results are shown in Table 2.

TABLE 2

	Initial Optical Density ¹					Optical Density @ 15 Minute Water Soak				
	CMY	C	M	Y	K	CMY	C	M	Y	K
Example 2	1.3 4	1.0 4	1.0 8	0.7 6	1.3 7	1.3 3	1.0 7	1.0 4	0.8 1	1.4 2
Example 3	1.3 3	0.9 9	1.0 3	0.7 3	1.3 3	1.3 4	1.0 7	1.0 6	0.7 8	1.3 7
Example 4	1.3 6	1.0 4	1.0 9	0.7 7	1.3 8	1.3 3	1.0 5	1.0 2	0.7 9	1.3 7
Example 5	1.2 1	1.1 1	1.1 9	0.8 7	1.2 0	1.2 3	1.1 8	1.1 9	0.9 2	1.2 2

Example 6

- 46 -

[00151] A 9.22% solids by weight solution of WitcoBond 234 was applied to a Teslin® TS1000 substrate using a metering bar as described in Examples 2-5. Immediately thereafter, a 5.78% solids by weight solution of CinFix NF was similarly applied to the substrate. The coated Teslin® TS1000 was then dried at 95°C for 2 minutes. The dried sheet was removed from the oven and the same coating procedure was repeated on the opposite side of the sheet. A test print pattern was printed on the coated Teslin® using an HP970 Inkjet Printer as described in Examples 2-5. Based on visual inspection, the printed image demonstrated excessive ink bleeding and poor drying properties.

Example 7

[00152] A coating composition was prepared by diluting in a stainless steel mix tank under high speed mixing with an overhead mixer, a 61.5% solids by weight anionic polyurethane dispersion sold under the trade name WitcoBond® 234 available from Crompton Corporation, Greenwich, Connecticut, to 9.22% solids by weight. In a separate feed tank a 55% solids by weight solution of a polyamide amine reacted with epichlorohydrin sold under the trade name CinFix NF by Stockhausen GmbH & Co. KG, Krefeld, Germany, was diluted to 5.78% solids by weight. The WitcoBond 234 dispersion was added to the diluted CinFix NF solution. The resulting suspension demonstrated an unacceptably heavy precipitate which was a polysalt of the CinFix NF and WitcoBond 234.

Examples 8-10

[00153] Coating compositions were prepared as in Example 1 and were applied to silk fabric (0.10lb/sq yd, 5mil gauge), cotton fabric (0.34lb/sq yd, 13.6mil gauge) and a polypropylene/cellulose nonwoven substrate (0.14lb/sq yd, 9.5mil gauge). For each material coated, a sheet (8.5" x 11") was fixed to a 15" x 20" x 20 mil backing sheet. A metering

- 47 -

bar was placed 1 - 2 inches above the top of the sheet, parallel to the top edge. A 10 - 20 ml quantity of coating was drawn into a disposable plastic syringe. The coating was deposited as a bead strip (approximately 1/8 inches wide) directly next to and touching the metering bar. The bar was drawn completely across the sheet at a continuous/constant rate. The resultant wet sheet was placed in a forced air oven, secured and dried at 95°C for 2 minutes. The dried sheet was removed from the oven and the same coating procedure was repeated on the opposite side of the sheet. The sheet was then taped to a transparency sheet to provide rigidity and was then ready to be printed and tested. The coating compositions were applied with an approximate coat weight of 0.73 g/m² (total front and back). Coat weight was determined as previously described in Examples 2-5.

[00154] Examples 8 - 10 were printed with an ink jet printer, Model HP970 by Hewlett Packard Company, Palo Alto, California and compared to the same substrates without coating. After printing, each sheet was removed from the rigid transparency sheet. Coated and uncoated printed sheet types were soaked in water at ambient temperature for 5 days. Optical density was measured after 5 days of soaking. The optical density of cyan (C), magenta (M), yellow (Y), black (K) and composite black (CMY), were measured using a Model RD922, MacBeth ANSWER II Densitometer, manufactured by Kolimorgen Instrument Corporation, before and after water soak.

[00155] The recorded images for the coated substrates remained intact after 15 minutes, i.e., the ink did not bleed or the optical density of the image was not significantly decreased for each sample. The uncoated sheets bled immediately, completely washing away the printed image within the 15 minute soak time. The printed image on each of the coated substrate did experience ink bleed after 5-day water soak exposure, as seen by the optical density values. The

- 48 -

resultant printed images were faded but had good line sharpness and legible text.

	Initial Optical Density					Optical Density @ 5day Water Soak				
	CMY	C	M	Y	K	CMY	C	M	Y	K
Example 8	1.2 3	1.0 4	1.2 4	1.0 8	1.2 4	0.8 7	0.7 1	0.6 2	0.5 5	0.8 0
Silk (uncoated)	0.9 7	0.8 4	0.8 8	0.7 2	0.9 5	Color bars washed out/not measurable				
Example 9	1.2 6	1.1 3	1.3 1	1.1 1	1.2 7	0.8 1	0.6 9	0.7 6	0.5 4	0.9 2
Cotton (uncoated)	0.9 4	0.8 1	0.9 1	0.8 1	0.9 5	Color bars washed out/not measurable				
Example 10	1.4 2	1.1 9	1.4 6	1.1 1	1.4 6	1.1 4	0.8 9	0.6 7	0.5 8	1.2 1
Polypropylen/ Cellulose (uncoated)	1.2 6	1.1 5	1.4 3	1.0 6	1.2 9	Color bars washed out/not measurable				

Example 11

[00156] A coating composition designated herein as "01" was prepared as follows. In a mixing vessel under high speed mixing with an overhead mixer, a 61.5% solids by weight anionic polyurethane dispersion sold under the trade name Witcobond W-234 available from Crompton Corporation, Greenwich, Connecticut, was diluted with deionized water to a 10.0% solids by weight dispersion. In a separate vessel, a 55% solids by weight solution of a polyamide amine reacted with epichlorohydrin sold under the trade name CinFix NF available from Stockhausen GmbH & Co. KG, Krefeld, Germany, was diluted with deionized water to a 10.0% solids by weight solution, and was subsequently added to the diluted anionic polyurethane dispersion. The mixture was mixed for fifteen minutes following completion of the addition. The resulting

- 49 -

mixture contained 40 parts by weight of solids of CinFix NF and 60 parts by weight of solids of Witcobond W-234.

[00157] A second coating was prepared as above-described with the exception that CinFix NF was replaced on an equivalent dry solids basis with CinFix RDF. This second coating composition is referred to herein as 01/RDF. CinFix RDF is a water solution of poly(diallyl dimethyl ammonium chloride) at 31% solids commercially available from Stockhausen GmbH & Co. KG, Krefeld, Germany. The CinFix RDF was diluted to 10.0% solids by weight prior to addition to the Witcobond W-234.

[00158] A third coating was prepared as above-described for the "01" composition with the exception that CinFix NF was replaced on an equivalent dry solids basis with diallyldimethylammonium chloride. This third coating composition is referred to herein as "01/DADMAC". Diallyldimethyl ammonium chloride is commercially available from Aldrich Chemical Company of Milwaukee, WI, as a 65% solution in water. It was diluted to 10.0% solids by weight prior to addition to the Witcobond W-234.

[00159] A fourth coating was prepared as above-described for the "01" composition with the exception that CinFix NF was replaced on an equivalent dry solids basis with the reaction product of equimolar amounts of diethyl amine and epichlorohydrin at 30% solids in water. This fourth coating composition is referred to herein as "01/DEA-EPI". The reaction product was not completely miscible with water in the 30/70 parts by weight mix necessary for 30% solids and therefore, was acidified to a pH of 5 with acetic acid to render it soluble in water for use in the coating. It was diluted to 10.0% solids prior to addition to the Witcobond W-234.

[00160] Sheets of Teslin® TS1000 and SP1000 were coated on both sides with each of the above-mentioned coatings using a #9 rod. The coating was applied to the front surface, dried

- 50 -

for a period of two minutes at a temperature of 95°C, and then applied to the back surface and dried for two minutes at 95°C. The finished sheets were then printed with a pattern on a Hewlett-Packard 960C printer at "HP Premium Photo Paper - Glossy" setting. The color density of the printed color bar section of the pattern was measured using an X-Rite Model 418 Densitometer, calibrated on a white tile standard. The printed color bar section was cut out of each sheet and immersed in a beaker of de-ionized water overnight (i.e., 14 hours). The sections were then removed from the water baths and allowed to air dry for a period of four hours. The color density after soak was then measured.

[00161] The results are shown in the following table:

Coating	Substrate	Soak	CMY	C-100	M-100	Y-100	K-100
"01"	TS1000	No	1.31	1.23	1.24	0.93	1.31
"01"		Yes	1.33	1.16	1.20	0.92	1.33
"01"	SP1000	No	1.32	1.23	1.25	0.93	1.32
"01"		Yes	1.32	1.16	1.19	0.90	1.33
"01/RDF"	TS1000	No	1.52	1.10	1.20	0.88	1.55
"01/RDF"		Yes	1.54	1.04	1.10	0.84	1.55
"01/RDF"	SP1000	No	1.16	0.97	1.28	0.99	1.20
"01/RDF"		Yes	1.13	0.91	1.21	1.00	1.15
"01/DADMAC"	TS1000	No	1.73	1.13	1.01	0.82	1.80
"01/DADMAC"		Yes	1.53	0.11	0.17	0.13	1.55
"01/DADMAC"	SP1000	No	1.37	0.91	1.44	1.06	1.58
"01/DADMAC"		Yes	0.26	0.14	0.20	0.15	0.16
"01/DEA-EPI"	TS1000	No	0.81	0.98	0.85	0.57	0.81
"01/DEA-EPI"		Yes	0.60	0.66	0.36	0.24	0.59
"01/DEA-EPI"	SP1000	No	0.75	0.92	0.82	0.55	0.76
"01/DEA-EPI"		Yes	0.54	0.62	0.35	0.23	0.55

[00162] The "01" coating on either substrate exhibited acceptable color density and water resistance and there was no visual evidence of color bleed. Based on visual inspection, the printed images were crisp and clear. The "01/RDF" coating also demonstrated acceptable color density and water resistance, showing no visual bleed. However, based on visual inspection there was a slight "feathering" or blurring of the image on the SP1000 substrate. The "01/DADMAC" coating had high color density before the soak, but based on visual inspection, the inks did not completely dry on the surface and

- 51 -

were almost completely removed from both of the substrates during the soak. Further, based on visual inspection, the images were not distinct, there was significant color bleed and the images were not clear. The "01/DEA-EPI" coating had low color density on both substrates and the water resistance was poor. Based on visual inspection, there was no color bleed and the images were clear but appeared faded.

Example 12

[00163] One coated Teslin® sheet was placed on top of one 20-inch x 25-inch sheet of 0.10-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. Below the PVC ply was a second ply of 20-inch x 25-inch x 10mil PVC, cut grain short. Below the 10mil PVC grain short ply was a 20-inch x 25-inch x 2mil PVC sheet of Klockner ZE84 cut grain long. A sheet 21-inch x 26-inch of 2-mil clear polyester was placed over the Teslin® sheet to act as a release liner. This construction was placed between two 21" x 26" x 30mil polished stainless steel metal plate. An identical polyester/treated Teslin® sheet/PVC/PVC/PVC lay-up was placed on top of a stainless plate from the existing construction. A polished metal plate was placed over the exposed polyester release liner. The pattern was repeated ten more times so that twelve pre-pressed multi-layer plys existed in the stack. The resultant stack was placed between buffer pads. The buffer pads are a combination polyamide fiber and mechanical rubber, manufactured and supplied by Yamauchi Corporation, designed to more uniformly distribute temperature and press during thermal lamination. The resultant stack plus buffer pads was then placed between two slightly larger 125mil un-polished non-corrosive metal plates. This entire construction, referred to as a book, was placed in a TMP laminating press, preheated to 300°F. The composite construction was compression laminated at a pressure of 203psi. The entire book was held

- 52 -

under this condition until the middle ply's of the book reached a temperature of 261°F. Then while still under press, the platens were cooled long enough to allow the same center plys to reach 100°F. After being removed from the press, all twelve composite sheets were removed from the book. All twelve composite sheets were topically treated with static guard on the pvc surface. All twelve finished composite sheets had good integrity; any attempt to delaminate destroyed the Teslin® layer, which demonstrated a good adhesive and seamless bond between the Teslin® and the PVC. ISO7910 ID-1 cards were die cut using PMC high die equipment with the Teslin® surface facing the cutting blade of the die. The finished cards from each composite sheet had good integrity and good lat flat. The resultant cards blocked slightly and did not demonstrate required slip performance.

Example 13

[00164] Coating composition Wikoff SCW 4890, manufactured and supplied by Wikoff Industries was applied to 300ft of 2mil Klockner ZE84 pvc sheet using a flexographic or gravure coating method. A single coating station was fixtured with a 6bcm anilox roll and non-textured rubber application roll. The coating feed chamber was supplied from a coating holding tank and pump. Continuous roll stock was threaded through the equipment so that the coated sheet passed through a drying oven, with the coated surface facing the hot air source. The line speed was 200fpm, oven temperature was 105°C (220°F) and a single coating pass was applied. The coating composition was applied with an approximate coat weight of 6.1mg/sqin. The resultant coated roll was converted into 20" x 25" sheets, grain long.

Example 14

- 53 -

[00165] The 2mil coated pvc sheet prepared as described in Example 13 was fabricated into cards using the following procedure. One coated Teslin® sheet was placed on top of one 20-inch x 25-inch sheet of 0.10-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. Below the PVC ply was a second ply of 20-inch x 25-inch x 10mil PVC, cut grain short. Below the 10mil PVC grain short ply was the coated 20-inch x 25-inch x 2mil PVC sheet cut grain long, positioned with the coated surface facing away from the adjacent 10mil pvc ply. A sheet 21-inch x 26-inch of 2-mil clear polyester was placed over the Teslin® sheet to act as a release liner. This construction was placed between two 21" x 26" x 30mil polished stainless steel metal plate. An identical polyester/treated Teslin® sheet/PVC/PVC/PVC lay-up was placed on top of a stainless plate from the existing construction. A polished metal plate was placed over the exposed polyester release liner. The pattern was repeated ten more times so that twelve pre-pressed multi-layer plys existed in the stack. The resultant stack was placed between buffer pads. The buffer pads are a combination polyamide fiber and mechanical rubber, manufactured and supplied by Yamauchi Corporation, designed to more uniformly distribute temperature and press during thermal lamination. The resultant stack plus buffer pads was then placed between two slightly larger 125mil un-polished non-corrosive metal plates. This entire construction, referred to as a book, was placed in a TMP laminating press, preheated to 300°F. The composite construction was compression laminated at a pressure of 203psi. The entire book was held under this condition until the middle ply's of the book reached a temperature of 261°F. Then while still under press, the platens were cooled long enough to allow the same center plys to reach 100°F. After being removed from the press, all twelve composite sheets were removed from the book. All

- 54 -

twelve finished composite sheets had good integrity; any attempt to delaminate destroyed the Teslin® layer, which demonstrated a good adhesive and seamless bond between the Teslin® and the PVC. ISO7910 ID-1 cards were die cut from the each of the 20-inch x 25-inch x 30.5mil composite sheets. The finished cards from each composite sheet had good integrity and good lat flat. The resultant cards demonstrated non-blocking behavior and required slip performance.

[00166] Friction Force Test Method

A card was fixed to a smooth flat base.

A second card was placed on top of the base card, with an offset of ½-inch over the long edge.

The second card was attached to a force gauge through a cable and pulley system. The force gauge was fixed to the travel arm of an instron.

A symmetrical weight was placed on the second card with the back edge of the weight centered and flush with the trailing edge of the second card.

The card pair was staged one (1) minute prior to pulling.

The top card was slid over the bottom card approximately 1.5-inch and the maximum pull force measured on the force gauge was recorded.

The procedure was repeated five (5) times, each time with a different card pair.

The average, standard deviation and % coefficient of variation of all six measurements were calculated and reported.

Card Slip Performance

Friction Force Measurements	Uncoated	4890/1pass	4890/2passes
1kg load results	1.33	1.105	0.984

- 55 -

(lb.)			
Std dev.	0.073	0.192	0.068
%COV	5.5	17.4	6.9
200g load results (lb.)	0.284	0.179	0.144
Std. Dev.	0.036	0.027	0.014
%COV	12.6	15.1	9.79

Example 15

[00167] One coated Teslin® sheet was placed on top of one 20-inch x 25-inch sheet of 0.10-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. Below the PVC ply was a second ply of 20-inch x 25-inch x 10mil PVC, cut grain short. Below the 10mil PVC grain short ply was a 20-inch x 25-inch x 2mil PVC sheet of Klockner ZE84 cut grain long. A sheet 21-inch x 26-inch of 2-mil clear polyester was placed over the Teslin® sheet to act as a release liner. This construction was placed between two 21" x 26" x 30mil polished stainless steel metal plate. An identical polyester/treated Teslin® sheet/PVC/PVC/PVC lay-up was placed on top of a stainless plate from the existing construction. A polished metal plate was placed over the exposed polyester release liner. The pattern was repeated ten more times so that twelve pre-pressed multi-layer plys existed in the stack. The resultant stack was placed between buffer pads. The buffer pads are a combination polyamide fiber and mechanical rubber, manufactured and supplied by Yamauchi Corporation, designed to more uniformly distribute temperature and press during

- 56 -

thermal lamination. The resultant stack plus buffer pads was then placed between two slightly larger 125mil un-polished non-corrosive metal plates. This entire construction, referred to as a book, was placed in a TMP laminating press, preheated to 300°F. The composite construction was compression laminated at a pressure of 203psi. The entire book was held under this condition until the middle ply's of the book reached a temperature of 261F. Then while still under press, the platens were cooled long enough to allow the same center plys to reach 100°F. After being removed from the press, all twelve composite sheets were removed from the book. All twelve composite sheets were topically treated with static guard on the pvc surface. All twelve finished composite sheets had good integrity; any attempt to delaminate destroyed the Teslin® layer, which demonstrated a good adhesive and seamless bond between the Teslin® and the PVC. ISO7910 ID-1 cards were die cut from the each of the 20-inch x 25-inch x 30.5mil composite sheets. The finished cards from each composite sheet had good integrity and good lat flat. The resultant cards demonstrated non-blocking behavior and required slip performance. These cards did, however, block when placed in a 100card stack following exposure to 24hours, 85% RH, 55C, under a 1 kg. load. Any attempt to delaminate destroyed the Teslin® layer, which demonstrated a good adhesive and seamless bond between the Teslin® and the PVC.

Lamination Plate Build-up & Friction Force vs.
PVC Surface Treatment

Sample ID	2mil PVC surface treatment (Anilox Roll/Chemistry)	Initial 1kg Friction Force (lb.)	Friction Force following 85%RH/55C/1kg /24hrs (lb.)	Build-up/Lamination Cycles
Uncoated	Not Applicable	>2.0	Cards Blocked	No residue/build-up
8181-92-	6bcm/solid	0.728	0.851	Heavy /

- 57 -

01	roll/4890/1pass			2cycles
8181-92-02	5bcm/solid roll/4890/1pass	0.669	0.859	Slight / 3cycles
8181-92-04	5bcm/solid roll/75/25- 1124/4890blend/1pa ss	0.888	0.938	Very Slight / 3cycles
Lot #24	Laminates topically treated with DMDTAC	0.721	Cards blocked	No residue/build -up

[00168] Teslin® Coating Method (25 Gallon Mix)

<u>Ingredients</u>	<u>Amounts</u>
CinFix RDF	13.46kg
Deionized Water	24.98kg
PPG WC-71-2134	12.24kg
Deionized Water	16.74kg
Witcobond W240	12.17kg
Deionized Water	16.65kg

Mix Procedure

- Added specified amount of CinFix RFD to the main mix container and stirred.
- Added specified amount of DI water to the CinFix RFD and stirred for 10 minutes prior to the next premix addition. Continued to stir throughout the entire mix procedure.
- Added specified amount of PPG WC-71-2134 to a premix container and stirred.
- Added specified amount of DI water to the PPG WC-71-2134 and stirred for 10 minutes.
- Added PPG WC-71-2134 premix to the main mix container.
- Added specified amount of Witcobond W240 to a premix container and stirred.

- 58 -

- Added specified amount of DI water to the PPG WC-71-2134 and stirred for 10 minutes.
- Added Witcobond W240 premix to the main mix container.
- Stirred the final mix for 15 minutes.
- Measured/Monitored solids, pH and viscosity and made any necessary adjustments.

Coating composition given in a descriptive format:

Coating Description: 40 active parts CinFix RDF
30 active parts PPG WC-71-2134
30 active parts Witcobond W240
12.5% Total Mix Solids

Example 16

[00169] A coating of Wikoff SCW 4890, manufactured and supplied from Wikoff Industries was applied to 3,660 feet of 2 mil gauge Magnetic Stripe Master Roll, manufactured and supplied from JCP, using a flexographic/gravure coating method. A single coating station was fitted with a 5bcm anilox roll and non-textured rubber application roll. The coating feed chamber was supplied from a coating holding tank and pump. Continuous roll stock was threaded through the equipment such that the surface containing the magnetic stripe tape would receive the coating. Also the coated sheet passed through a drying oven, with the coated surface facing the hot air source. The line speed was 300fpm; oven temperature was 105°C (220°F); and a single coating pass was applied. A gentle curtain of air was directed towards the continuous coated sheet just prior to the wind-up station to eliminate folds and wrinkles. The coating was applied with an approximate coat weight of 5mg/sqin. The resultant coated roll was converted into 25" x 20" sheets, grain short.

- 59 -

Example 17

[00170] The 2 mil coated Magnetic Stripe Master Sheet prepared as described in Example 16 was fabricated into cards using the following procedure. One coated Teslin® sheet was placed on top of one 20-inch x 25-inch sheet of 0.10-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. Below the PVC ply was a second ply of 20-inch x 25-inch x 10 mil PVC, cut grain long. Below the 10 mil PVC grain long ply was the coated 20-inch x 25-inch x 2mil Magnetic Stripe Master Sheet cut grain short, positioned with the coated surface facing away from the adjacent 10 mil pvc ply. A sheet 21-inch x 26-inch of 2-mil clear polyester was placed over the Teslin® sheet to act as release liner. This construction was placed between two 21" x 26" x 30 mil polished stainless steel metal plate. An identical polyester/treated Teslin® sheet/PVC/PVC/Magnetic Stripe Master Sheet lay-up was placed on top of a stainless plate from the existing construction. A polished metal plate was placed over the exposed polyester release liner. The pattern was repeated ten more times so that twelve pre-pressed multi-layer plies existed in the stack. The resultant stack was placed between buffer pads. The buffer pads are a combination polyamide fiber and mechanical rubber, manufactured and supplied by Yamauchi Corporation, designed to more uniformly distribute temperature and press during thermal lamination. The resultant stack plus buffer pads was then placed between two slightly larger 125mil un-polished non-corrosive metal plates. This entire construction, referred to as a book, was placed in a TMP laminating press, preheated to a temperature of 300°F. The composite construction was compression laminated at a pressure of 203 psi. The entire book was held under this condition until the middle plies of the book reached a temperature of 261°F. While still hot, the press was released from all books for one minute then the

- 60 -

pressure was re-introduced. The platens were cooled long enough to allow the same center plies to reach a temperature of 100°F. After being removed from the press, all twelve composite sheets were removed from the book. The mylar release liner was removed from the Teslin® sheet. The magnetic stripe surface showed defects resulting from print-off of the Wikoff coating onto the lamination plate. All twelve finished composite sheets had good integrity; any attempt to delaminate the article resulted in destroying the Teslin® layer, which demonstrated a good adhesive and essentially seamless bond between the Teslin® and the PVC. ISO7910 ID-1 cards were die cut from each of the 20-inch x 25-inch x 30.5 mil composite sheets. The finished cards from each composite sheet had good integrity and good lat flat. The resultant cards demonstrated non-blocking behavior and good slip performance.

Example 18 - Thermal Lamination

[00171] A sheet of TS 1000 (which was available from PPG Industries, Incorporated, under the trade name Teslin) measuring 8.5 x 11 inches was cut from a master roll. The Teslin sheet was coated using four (4) passes on each side. The coating composition used to coat the Teslin was prepared by first diluting a 31% solids anionic polyurethane sold under the trade name WitcoBond 234 (available from Crompton Corporation, Greenwich, Connecticut), to 12.3% solids in a stainless steel mix tank under high speed mixing with an overhead mixer. In a separate feed tank a 55% solids solution of a polyamide amine reacted with dimethylamine and epichlorohydrin (available under the trade name CinFix NF by Stockhausen GmbH & Co. KG, Drefeld, Germany), was diluted to 7.7% solids and then subsequently added to the diluted anionic polyurethane dispersion, at a 50/50 volume ratio, and the mixture was mixed for 15 minutes. The pH was adjusted to 5.0 +/- 0.5. The total resin solids of the mixture was 10%.

- 61 -

[00172] The coating composition was applied to the sheet of Teslin (10 mil thick) using flexographic coating technology which included two coating stations containing forced air drying ovens. Each coating station consisted of a coating feed chamber, anilox roll and rubber roll. The coating feed chamber was supplied from a coating holding tank and pump. Only one coating station was used in the preparation of this material. The apparatus was fitted with a 7 bcm (billion cubic microns) anilox roll, the line speed was 180 fpm (feet per minute), and the oven temperature was 105°C (220°F). Eight (8) passes per roll were made, which corresponds to four (4) passes per surface.

[00173] A test print was then printed onto the sheet using an HP1220C color inkjet printer. The printed sheet was laminated using the following lamination peel strength test method. The 8.5 x 11 inch sheet of Teslin was covered with an 8.5 x 11 inch Sealtran 3/2 laminating film. A 2 x 11 inch strip of 20 lb. bond paper was placed along the center line (in the 11 inch direction) on the Teslin. The film to be tested was cut to 8.5 inch by 11 inch and placed directly on top of the aforementioned structure. The laminated sheet was cut into a piece 4.25 inches by 11 inches. Strips were then cut (1 inch by 4.25 inches) using a JDC Precision Sample Cutter (Thwing Albert Instruments). Each strip was placed in a silicone-coated "laminating pocket". The pocket was fed through a pocket laminator large enough to accommodate the pocket. The laminating roll temperature varied within a range of from 275 to 300°F (120-135°C). The laminated samples were then stored at room temperature for at least 24 hours prior to peel testing. The laminating film was peeled back from the Teslin and placed into the top jaw of a tensile tester. The bottom portion was placed into the bottom jaw of the tensile tester. A 180° peel was performed at 0.5 inches/minute with a sample rate of 4.0 pt./second. The test results showed the

- 62 -

initial peel strength was 9.6 lbs./inch and demonstrated that the resulting substrate retained its integrity following a 24 hour water soak.

Example 19

[00174] In preparing a coating composition of the present invention, a 31% polydimethyldiallylammonium chloride sold under the trade name CinFix RDF available from Stockhausen GmbH & Co. KG, Krefeld, Germany was diluted to 10% with deionized water in a stainless steel or polyethylene mix vessel under mild agitation. Mild agitation defined by a medium pitch three lobed mixing head, the system at a mix-head to mix vessel diameter ratio of 1 to 3 and the mix-head spinning at 600 - 1000 rpm and appropriately positioned. In a separate mix container, a 29% aqueous cationic acrylic solution sold under the name WC-71-2143 available from PPG Industries, Inc. is diluted with deionized water to 10% and added to the main mix vessel containing pre diluted CinFix RDF. In a separate mix container, a 30% aqueous cationic polyurethane dispersion sold under the trade name Witcobond W240 available from Crompton Corporation is diluted with deionized water to 10% and added to the main mix vessel containing the CinFix RDF and PPG WC-71-2143 mixture. The resultant coating composition is stirred for 15 minutes. The resultant pH was 5.5 +/- 0.5. The total solids of the composition was 10% and a viscosity of 56cps measured using a Brookfield viscometer, RVT, spindle no. 1, at 50 rpm and 25°C.

[00175] For comparison, other coating compositions were produced using alternate CinFix additives and polyurethane dispersions with or without WC-71-2143.

- 63 -

Ingredients	% solids	8181-67-01	-02	-03	-04	-05	-06	-07	-08	-09
CinFix NF	51	18.5	-	-	-	-	-	-	-	-
CinFix 167	10	-	100	100	100	100	-	-	-	-
CinFix RDF	10	-	-	-	-	-	100	100	100	100
WitcoBond W-234	31	49.6	-	-	-	-	-	-	-	-
WitcoBond X-051	10	-	150	75	-	-	150	75	-	-
WitcoBond W-240	10	-	-	-	150	75	-	-	150	75
WC-71-2143	10	-	-	75	-	75	-	75	-	75

[00176] All values are in parts by weight (pbw).

Ingredients:

CinFix NF - a 50-60% active aqueous solution of poly(quaternary amine) polymer (CAS No. 68583-79-9) from Stockhausen GmbH & Co. KG, Krefeld, Germany.

CinFix 167 - a 50-60% active aqueous solution of poly(quaternary amine) (Composition -Trade Secret) from Stockhausen GmbH & Co. KG, Krefeld, Germany.

CinFix RDF - a 30-35% active aqueous solution of poly(quaternary amine) polymer (CAS No. 26062-79-3) from Stockhausen GmbH & Co. KG, Krefeld, Germany.

WitcoBond W-234 - a 30-35% solids water-based dispersion of an anionic aliphatic urethane from Uniroyal Chemical of Middlebury, CT.

WitcoBond X-051 - a 30-35% solids water-based dispersion of a cationic urethane from Uniroyal Chemical of Middlebury, CT.

WitcoBond W-240 - a 30-35% solids water-based self-cross linking anionic polyurethane dispersion from Uniroyal Chemical of Middlebury, CT.

WC-71-2143 - a 25-30% solids aqueous dispersion of a cationic acrylic polymer from PPG Industries of Pittsburgh, PA.

PPG formulation no. WC-71-2143 is as an aqueous secondary amine and hydroxyl functional acrylic polymer prepared via

- 64 -

solution polymerization. Also described as a cationic acrylic polymer aqueous dispersion. WC-71-2143 was prepared as follows.

<u>Ingredients</u>	<u>Weight, grams</u>
<u>Initial Charge</u>	

Isopropanol	130.0
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Feed 1

Isopropanol	113.0
n-Butyl acrylate	69.2
Methyl methacrylate	153.0
2-(tert-Butylamino)ethyl methacrylate (CAS 3775-90-4)	73.0
Styrene	69.2
VAZO® 67 Initiator ¹	18.2

Feed 2

Glacial Acetic Acid	17.7
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Feed 3

Deionized Water	1,085.0
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¹ 2, 2'-Azobis(2-methylbutanenitrile) initiator commercially available from E. I. du Pont de Nemours and Company, Wilmington, Delaware

[00177] The initial charge was heated in a reactor with agitation to reflux temperature (80°C.). The Feed 1 was added in a continuous manner over a period of 3 hours. At the completion of Feed 1 addition, the reaction mixture was held

- 65 -

at reflux for 3 hours. The resultant acrylic polymer solution had a total solids content of 61.7 percent (determined by weight difference of a sample before and after heating at 110°C. for one hour) and number average molecular weight of 4792 as determined by gel permeation chromatography using polystyrene as the standard. Thereafter, Feed 2 was added over five minutes at room temperature with agitation. After the completion of the addition of Feed 2, Feed 3 was added over 30 minutes while the reaction mixture was heated for azeotropic distillation of isopropanol. When the distillation temperature reached 99°C, the distillation was continued about one more hour and then the reaction mixture was cooled to room temperature. The total distillation collected was 550.6 grams. The product, which was a cationic acrylic polymer aqueous solution, had a solids content of 32.6 percent by weight (determined by weight difference of a sample before and after heating at 110°C. for one hour), and a pH of 5.25.

All % solids values are % by weight.

[00178] Coatings were applied to blank 8½" x 11" Teslin® TS 1000 sheet. Coating weight is measured by difference using an electronic balance.

- The blank sheet is weighed.
- Coating is applied to the front side using a #9 wire-wrapped rod.
- The sheet is baked at 95° C in a textile oven (Model LTF from Werner Mathis AG, Zurich, Switzerland) for 2 minutes.
- The sheet is removed from the oven and coating is applied to the backside using a #9 wire-wrapped rod.
- The sheet is re-baked at 95° C in the textile oven for 2 minutes.
- The sheet is removed, allowed to cool to the touch and reweighed.

- 66 -

- Coating weight in milligrams/square-inch is determined by dividing weight difference in milligrams by coated area.

[00179] The dynamic viscosity of the mixed coatings was measured using a #2 Zahn cup and the static viscosity was measured using a Brookfield Model DV-1+ viscometer using a #2 spindle at 100 rpm.

Coating Coating Weight #2ZahncupBrookfieldViscosity
mg./square inch(seconds) (Centipoise @ 22°C)

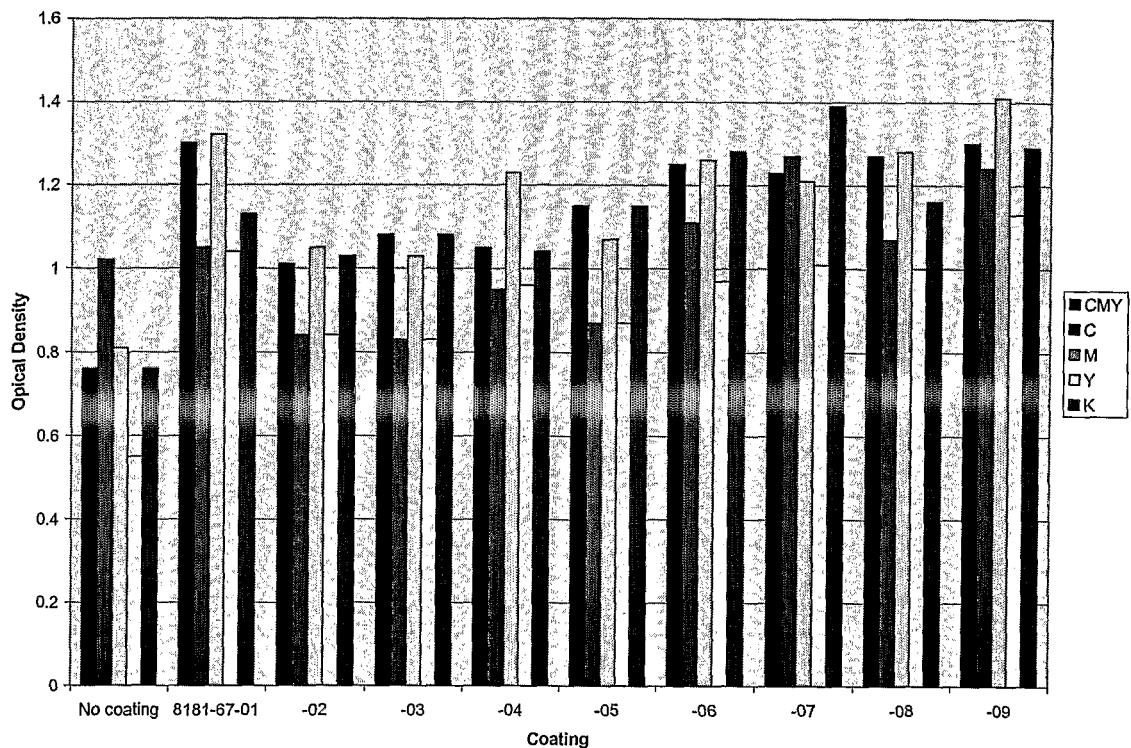
-01	2.5	16.5	51.6
-02	0.4	23.6	236.4
-03	0.9	17.7	65.6
-04	1.5	15.5	40
-05	0.3	21.1	85.6
-06	0.4	21.7	125.2
-07	0.9	16.1	40.8
-08	0.6	16.3	48.8
-09	1.1	15.4	41.2

[00180] Test prints from the coated Teslin sheets were generated off of an HP960C printer, set to normal default print mode. Optical density values were measured using an X-Rite® densitometer, model type 418, normalized against a Macbeth® black/white standard plate. Test prints were also generated using uncoated Teslin TS1000 for comparison. Optical density values are listed in the following table.

Coating	CMY	C	M	Y	K
No coating	0.76	1.02	0.81	0.55	0.76
-01	1.30	1.05	1.32	1.04	1.13

- 67 -

-02	1.01	0.84	1.05	0.84	1.03
-03	1.08	0.83	1.03	0.83	1.08
-04	1.05	0.95	1.23	0.96	1.04
-05	1.15	0.87	1.07	0.87	1.15
-06	1.25	1.11	1.26	0.97	1.28
-07	1.23	1.27	1.21	1.01	1.39
-08	1.27	1.07	1.28	1.00	1.16
-09	1.30	1.24	1.41	1.13	1.29



[00181] The 09 coating was applied to 8½" x 11" sheets of Teslin® TS1000 and SP1000 and cured as described above. Test prints from the coated Teslin sheets were generated off of an HP960C printer, set to normal default print mode. Optical density values were measured using an X-Rite® densitometer, model type 418, normalized against a Macbeth® black/white standard plate. Optical density values are listed in the following table.

- 68 -

Teslin	CMY	C	M	Y	K
TS1000	1.08	1.20	1.23	0.99	1.16
SP1000	1.09	1.22	1.22	1.02	1.16

Example 20

[00182] Several 6,600ft rolls of 10.5mil Teslin TS1000 were sized with coating composition described in Example 19 in accordance the technique described in Example 19. The resultant rolls was converted into 8.5" x 11" sheets, grain long. Test prints were generated off of an HP960C printer, set to best ink jet photo grade matte finish. Both sides of the substrate were printed. The optical density of color bars representing the five primary color/ink types: composite black, cyan, magenta, yellow and pigment black were measured. The printed color bars were submerged in tap water for 15minutes and the resultant optical densities measured. The procedure was then repeated after a total of 24hours of continuous soaking. The optical density values are given in the following tables.

Optical Density Retention - Side A
24hrs, Tap Water

Water Soak Time	CMY	Cyan	Magenta	Yellow	Pigment Black
Initial	1.31	1.13	1.26	0.88	1.30
15 minutes	1.31	1.14	1.25	0.90	1.30
24 hours	1.32	1.12	1.24	0.89	1.29

Optical Density Retention - Side B

- 69 -

24hrs, Tap Water

Water Soak Time	CMY	Cyan	Magenta	Yellow	Pigment Black
Initial	1.31	1.14	1.27	0.89	1.30
15 minutes	1.33	1.14	1.23	0.91	1.30
24 hours	1.29	1.10	1.23	0.90	1.29

[00183] All color bars remained solid after 24hours of soaking time in tap water. No bleed was visible off of any of the colors. Bold 10point font that was part of the test print samples, printed in composite black maintained good optical clarity.

Example 21

[00184] Sheets 26-inch x 38-inch of treated Teslin TS1000 substrate, 10.5mils thick, were cut from a master roll in the grain long direction. The Teslin had been coated with 3 passes on each side (3x3) using the same coating composition as described in Example 19 and the same Flexographic coating technology described in Example 19. One coated Teslin sheet was placed on top of one 26-inch x 38-inch sheet of 0.21-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. A sheet 27-inch x 39-inch of 2-mil clear polyester was placed over the Teslin sheet to act as a release liner. This release liner was removed from the composite sheet following lamination and is not an integral part of the final composite sheets. This construction was placed between two 27" x 39" x 30mil polished stainless steel metal plate. The resultant stack was then placed between two 27" x 39" x 125mil un-polished non-corrosive metal plates. This entire construction was placed

- 70 -

in a 200-Ton Wabash laminating press, preheated to 220°F. The composite construction was compression laminated at a pressure of 200psi for 8minutes at a temperature of 220°F. While under press, the platens were cooled to less than 100°F, which took approximately 22minutes. After being removed from the press, the resultant composite sheet was removed from the stack construction. The finished composite sheet had good integrity; any attempt to delaminate destroyed the Teslin layer, which demonstrated a good adhesive and seamless bond between the Teslin and the PVC. ISO7910 ID-1 cards were die cut from the resultant 26-inch x 38-inch x 30.5mil composite sheet. The finished cards had good integrity and good lat flat. Any attempt to delaminate destroyed the Teslin layer, which demonstrated a good adhesive and seamless bond between the Teslin and the PVC.

Example 22

[00185] Sheets 20-inch x 25-inch of treated Teslin substrate, 10.5mils thick, were cut from a master roll in the grain long direction. The Teslin had been coated with 3 passes on each side (3x3) using the same coating composition as described in example 1 and the same Flexographic coating technology described in example 2. One coated Teslin sheet was placed on top of one 20-inch x 25-inch sheet of 0.10-inch polyvinylchloride (PVC), supplied by Empire Plastics. The PVC sheet was cut in the grain long direction. Below the PVC ply was a second ply of 20-inch x 25-inch x 10mil PVC, cut grain short. Below the 10mil PVC grain short ply was a 20-inch x 25-inch x 2mil PVC sheet cut grain long. A sheet 21-inch x 26-inch of 2-mil clear polyester was placed over the Teslin sheet to act as a release liner. This construction was placed between two 21" x 26" x 30mil polished stainless steel metal plate. An identical polyester/treated Teslin sheet/PVC/PVC/PVC lay-up was placed on top of a stainless plate from the existing construction. A polished metal plate

- 71 -

was placed over the exposed polyester release liner. The pattern was repeated ten more times so that twelve pre-pressed multi-layer plys existed in the stack. The resultant stack was placed between buffer pads. The buffer pads are a combination polyamide fiber and mechanical rubber, manufactured and supplied by Yamauchi Corporation, designed to more uniformly distribute temperature and press during thermal lamination. The resultant stack plus buffer pads was then placed between two slightly larger 125mil un-polished non-corrosive metal plates. This entire construction, referred to as a book, was placed in a TMP laminating press, preheated to 300°F. The composite construction was compression laminated at a pressure of 203psi for 18minutes at a temperature of 300°F. While under press, the platens were cooled to less than 100°F, which took approximately 19minutes. After being removed from the press, all twelve composite sheets were removed from the book. All twelve finished composite sheets had good integrity; any attempt to delaminate destroyed the Teslin layer, which demonstrated a good adhesive and seamless bond between the Teslin and the PVC. ISO7910 ID-1 cards were die cut from the each of the 20-inch x 25-inch x 30.5mil composite sheets. The finished cards from each composite sheet had good integrity and good lat flat. Any attempt to delaminate destroyed the Teslin layer, which demonstrated a good adhesive and seamless bond between the Teslin and the PVC.

[00186] This foregoing example was also conducted using Teslin SP1000 which produced the same results as the Teslin TS1000.

Example 23

[00187] Composite sheets fabricated according to Example 19, were individually soaked in deionized water for 15minutes then allowed air dry for 24 hours. ISO7910 ID-1 cards were die cut

- 72 -

from the each of the 20-inch x 25-inch x 30.5mil composite sheets. The finished cards from each composite sheet had good integrity and good lat flat. Any attempt to delaminate destroyed the Teslin layer, which demonstrated a good adhesive and seamless bond between the Teslin and the PVC. Resultant conditioned cards demonstrated easier separation from a stack and slip characteristics compared to the unconditioned version.

[00188] The following table compares the optical density retention performance of the new offering (8181-67-09 recipe) to standard IJ1000WP (2 component recipe). Test print patterns used in this study were produced off of an HP970 color inkjet printer, set on best quality and photo grade ink jet glossy paper.

Optical Density following De-Ionized Water Soak

	Soak Time (hrs)	Composite Black	Cyan	Magenta	Yellow	Pigmented Black
Std. Teslin IJ1000WP	0	1.26	1.2	1.18	0.86	1.25
	24	1.21	1.13	1.03	0.74	1.19
	96	1.18	1.08	1.03	0.71	1.17
New Teslin IJ1000WP (8181-67-09)	0	1.39	1.33	1.22	0.91	1.37
	24	1.39	1.35	1.29	0.92	1.37
	96	1.39	1.32	1.31	0.92	1.36

[00189] The invention has been described with reference to specific embodiments. Obvious modifications and alterations will occur to others upon reading and understanding the

- 73 -

detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the invention or the equivalents thereof.

- 74 -

In the claims:

1. An ink jet recordable substrate coating composition having a pH less than 7 comprising:

- (a) an aqueous polyurethane dispersion; and
- (b) an aqueous solution of a nitrogen-containing polymeric dye fixative compound.

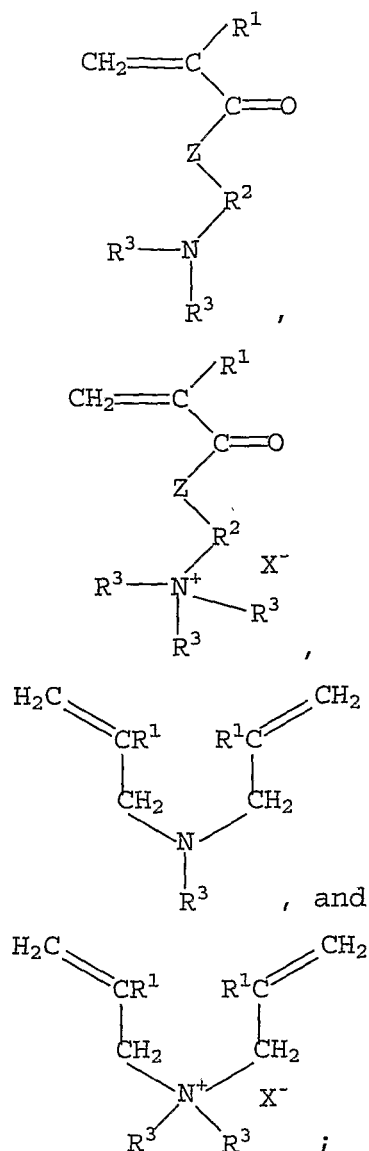
2. The ink jet recordable substrate coating composition of claim 1 wherein the polyurethane is selected from the group consisting of anionic polyurethanes, cationic polyurethanes, nonionic polyurethanes and mixtures thereof.

3. The ink jet recordable substrate coating composition of claim 2 wherein the aqueous anionic polyurethane dispersion comprises one or more anionic polyurethanes selected from the group consisting of aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, and aliphatic polycaprolactam polyurethanes.

4. The ink jet recordable substrate coating composition of claim 2 wherein the aqueous anionic polyurethane has one or more acid groups selected from the group consisting of carboxylic acid, sulfonic acid and mixtures thereof.

5. The ink jet recordable substrate coating composition of claim 1 wherein the aqueous solution of a nitrogen-containing polymeric dye fixative compound comprises a polymer comprising monomer residues derived from one or more nitrogen-containing monomers selected from the group consisting of:

- 75 -



wherein R^1 is selected independently for each occurrence in each structure from the group consisting of H and C_1 to C_3 aliphatic; R^2 is independently for each structure a divalent linking group selected from the group consisting of C_2 to C_{20} aliphatic hydrocarbon, polyethylene glycol and polypropylene glycol; R^3 is independently for each occurrence in each structure selected from the group consisting of H, C_1 to C_{22} aliphatic hydrocarbon and a residue from the reaction of the nitrogen with epichlorohydrin; Z is selected from the group consisting of -O- and -NR⁴-, where R^4 is selected from the

- 76 -

group consisting of H and CH₃; and X is selected from the group consisting of halides and methylsulfate.

6. The ink jet recordable substrate coating composition of claim 1 wherein the aqueous polyurethane dispersion is present at from 10 to 70 percent by weight of the ink jet recordable substrate coating composition and the aqueous solution of a nitrogen-containing polymeric dye fixative compound is present at from 30 to 90 percent by weight of the ink jet recordable substrate coating composition.

7. The ink jet recordable substrate coating composition of claim 1 prepared by mixing the nitrogen-containing polymeric dye fixative compound (b) into the aqueous polyurethane dispersion (a).

8. A method of coating an ink jet recordable substrate comprising:

- (a) providing an ink jet recordable substrate having a top surface and a bottom surface;
- (b) providing a coating composition having a pH less than 7 comprising:
 - (i) an aqueous polyurethane dispersion; and
 - (ii) an aqueous solution of a nitrogen-containing polymeric dye fixative compound;
- (c) applying the coating composition to at least one side of the ink jet recordable substrate.

9. The method of claim 8 wherein the ink jet recordable substrate comprises a microporous substrate having a top surface and a bottom surface and comprising:

- (a) a matrix comprising a polyolefin;
- (b) a finely divided particulate siliceous filler distributed throughout the matrix; and

- 77 -

(c) a network of interconnecting pores communicating throughout the microporous substrate, said pores constituting at least about 35 percent by volume of said microporous substrate.

10. The method of claim 9 wherein the polyolefin comprises one or both selected from the group consisting of a linear high molecular weight polyethylene having an intrinsic viscosity of at least 10 deciliters/gram and a linear high molecular weight polypropylene having an intrinsic viscosity of at least 5 deciliters/gram.

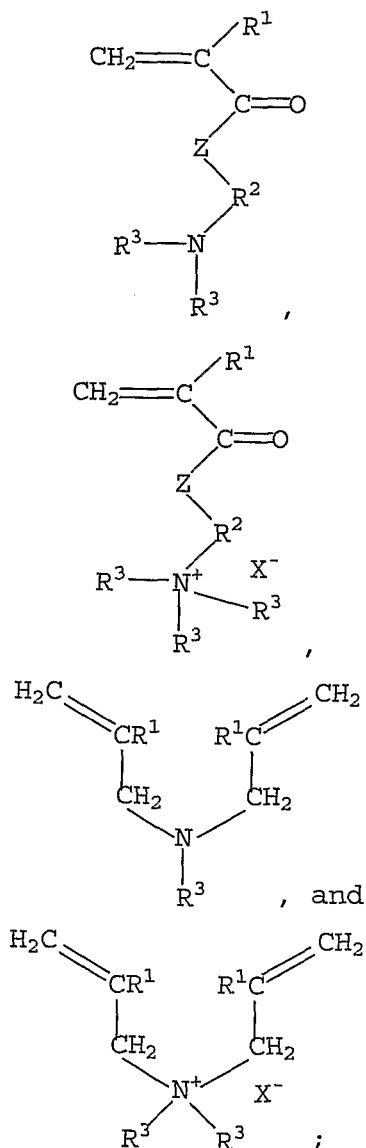
11. The method of claim 9 wherein the siliceous filler constitutes from 50 percent to 90 percent by weight of the microporous substrate.

12. The method of claim 8 wherein the aqueous polyurethane dispersion in (b)(i) comprises a polyurethane selected from the group consisting of anionic polyurethanes, cationic polyurethanes, nonionic polyurethanes, and mixtures thereof.

13. The method of claim 12 wherein the anionic polyurethane is selected from the group consisting of aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, and aliphatic polycaprolactam polyurethanes.

14. The method of claim 12 wherein the aqueous anionic polyurethane has one or more acid groups selected from the group consisting of carboxylic acid, sulfonic acid and mixtures thereof.

15. The method of claim 8 wherein the aqueous solution of a nitrogen-containing polymeric dye fixative compound comprises a polymer comprising monomer residues derived from one or more nitrogen-containing monomers selected from the group consisting of:



wherein R^1 is selected independently for each occurrence in each structure from the group consisting of H and C_1 to C_3 aliphatic; R^2 is independently for each structure a divalent linking group selected from the group consisting of C_2 to C_{20} aliphatic hydrocarbon, polyethylene glycol and polypropylene

- 79 -

glycol; R^3 is independently for each occurrence in each structure selected from the group consisting of H, C_1 to C_{22} aliphatic hydrocarbon and a residue from the reaction of the nitrogen with epichlorohydrin; Z is selected from the group consisting of -O- and -NR⁴-, where R^4 is selected from the group consisting of H and CH₃; and X is selected from the group consisting of halides and methylsulfate.

16. The method of claim 8 wherein the aqueous polyurethane dispersion is present at from 10 to 70 percent by weight of the ink jet recordable substrate coating composition and the aqueous solution of a nitrogen-containing polymeric dye fixative compound is present at from 30 to 90 percent by weight of the coating composition.

17. The method of claim 8 wherein the nitrogen-containing polymeric dye fixative compound is a polyamide amine reacted with epichlorohydrin.

18. The method of claim 8 wherein the coating composition has a total resin solids of from 1 to 35 wt.% based on the total weight of the coating composition.

19. The method of claim 8 wherein the aqueous polyurethane dispersion in (b)(i) comprises an anionic polyurethane and the coating composition is prepared by mixing the nitrogen-containing polymeric dye fixative compound (b)(ii) into the aqueous polyurethane dispersion (b)(i).

20. The method of claim 8 wherein the coating composition is applied to both sides of the ink jet recordable substrate.

21. A coated ink jet recordable substrate coated using the method of claim 8.

- 80 -

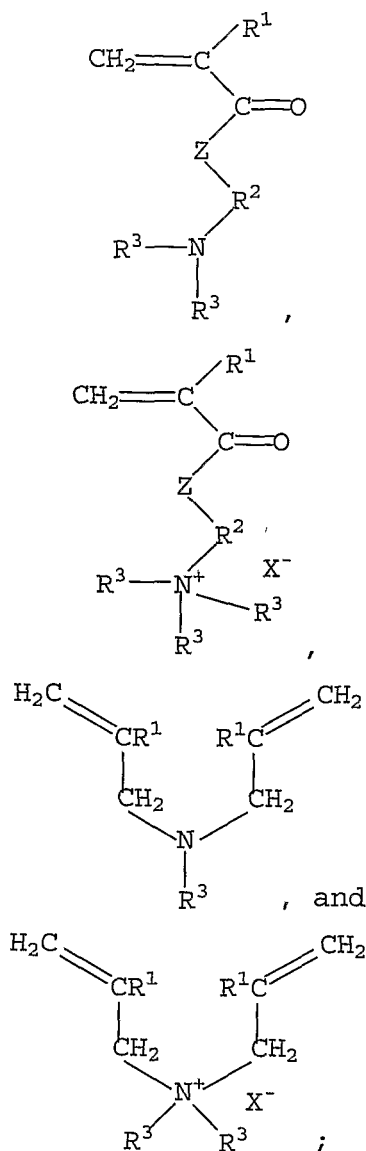
22. A coated microporous substrate comprising:

- (a) a microporous substrate having an upper surface and a lower surface comprising:
 - (i) a matrix comprising a polyolefin;
 - (ii) a finely divided particulate siliceous filler distributed throughout the matrix; and
 - (iii) a network of interconnecting pores communicating throughout the microporous substrate, said pores constituting at least about 35 percent by volume of said microporous substrate; and
- (b) a coating layer on at least one surface of the microporous substrate, said coating layer comprising:
 - (i) a polymeric nitrogen-containing dye fixative compound; and
 - (ii) one or more polyurethanes selected from the group consisting of anionic polyurethanes, cationic polyurethanes, nonionic polyurethanes, and mixtures thereof.

23. The coated microporous substrate of claim 22 wherein the polyurethane is an anionic polyurethane, and the aqueous anionic polyurethane has one or more acid groups selected from the group consisting of carboxylic acid, sulfonic acid and mixtures thereof.

24. The coated microporous substrate of claim 22 wherein the polymeric nitrogen-containing dye fixative compound comprises a polymer comprising monomer residues derived from one or more nitrogen-containing monomers selected from the group consisting of:

- 81 -



wherein R^1 is selected independently for each occurrence in each structure from the group consisting of H and C_1 to C_3 aliphatic; R^2 is independently for each structure a divalent linking group selected from the group consisting of C_2 to C_{20} aliphatic hydrocarbon, polyethylene glycol and polypropylene glycol; R^3 is independently for each occurrence in each structure selected from the group consisting of H, C_1 to C_{22} aliphatic hydrocarbon and a residue from the reaction of the nitrogen with epichlorohydrin; Z is selected from the group consisting of -O- and -NR⁴-, where R^4 is selected from the

group consisting of H and CH₃; and X is selected from the group consisting of halides and methylsulfate.

25. The coated microporous substrate of claim 22 wherein the polyurethane is present at from 10 to 70 percent by weight of the coating layer and the nitrogen-containing polymeric dye fixative compound is present at from 30 to 90 percent by weight of the coating layer.

26. The coated microporous substrate of claim 22 wherein the nitrogen-containing polymeric dye fixative compound is a polyamide amine reacted with epichlorohydrin.

27. The coated microporous substrate of claim 22 wherein the polyolefin comprises one or both selected from the group consisting of a linear high molecular weight polyethylene having an intrinsic viscosity of at least about 10 deciliters/gram and a linear high molecular weight polypropylene having an intrinsic viscosity of at least about 5 deciliters/gram.

28. The coated microporous substrate of claim 22 wherein the siliceous filler constitutes from 50 percent to 90 percent by weight of the microporous substrate.

29. The coated microporous substrate of claim 22 wherein the coating layer penetrates into at least the first 1 micron of the surface of the microporous substrate.

30. The coated microporous substrate of claim 22 wherein the microporous substrate has a thickness of from 0.5 to 100 mils.

31. The coated microporous substrate of claim 22 wherein the coat weight is from 0.001 g/m² to 50 g/m².

- 83 -

32. A multilayer article comprising an ink jet recordable substrate at least partially connected to a substantially nonporous material, said ink jet recordable substrate at least partially coated with a substantially water-resistant coating composition, and at least one of said ink jet recordable substrate and substantially nonporous material at least partially coated with a friction-reducing coating composition.

33. The multilayer article of claim 32 wherein said substantially water-resistant coating composition comprises:

- (a) an aqueous polyurethane dispersion; and
- (b) a cationic nitrogen-containing polymeric dye fixative material at least partially dissolved in an aqueous medium.

34. The multilayer article of claim 32 wherein said friction-reducing coating composition comprises a lubricant and a resin.

35. The multilayer article of claim 32 wherein said lubricant comprises polysiloxane.

36. The multilayer article of claim 32 wherein said resin comprises styrene acrylic polymer.

37. A method for producing a multilayer article comprising the steps of:

- (a) providing a ink jet recordable substrate having a top surface and a bottom surface;
- (b) providing a substantially water-resistant coating composition comprising a stable dispersion of:
 - (i) an aqueous polyurethane dispersion; and

- 84 -

(ii) a cationic nitrogen-containing polymeric dye fixative material at least partially dissolved in an aqueous medium;

(c) at least partially applying said coating composition to at least one surface of said ink jet recordable substrate;

(d) at least partially connecting said ink jet recordable substrate of (c) to a substantially nonporous material having a top surface and a bottom surface;

(e) providing a friction-reducing coating composition; and

(f) at least partially applying said friction-reducing coating composition to at least one surface of at least one of said ink jet recordable substrate and said substantially nonporous material.

38. A multilayer article comprising an ink jet recordable substrate, at least one substantially nonporous material and a magnetizable material.

39. The multilayer article of claim 38 wherein said magnetizable material is an oxide material.

40. The multilayer article of claim 39 wherein said oxide material is selected from ferrous oxide, iron oxide, and mixtures thereof.

41. The multilayer article of claim 38 wherein said magnetizable material is a slurry.

42. The multilayer article of claim 38 wherein said magnetizable material has a coercivity of from 200 to 5000.

43. The multilayer article of claim 38 wherein said magnetizable material is at least partially connected to at least one material selected from a protective material, a carrier material or an adhesive material.

44. The multilayer article of claim 43 wherein said protective material is selected from polyethylene terephthalate, polyester and combinations thereof.

- 85 -

45. The multilayer article of claim 43 wherein said carrier material is selected from polyethylene terephthalate, polyester and combinations thereof.

46. The multilayer article of claim 43 wherein said adhesive material is selected from polyvinyl acetate, starches, gums, polyvinyl alcohol, animal glues, acrylics, epoxies, polyethylene-containing adhesives, and rubber-containing adhesives.

47. The multilayer article of claim 43 wherein said protective material is at least partially connected to said magnetizable material, said magnetizable material is at least partially connected to said carrier material, and said carrier material is at least partially connected to said adhesive material.

48. The multilayer article of claim 38 wherein said magnetizable material is at least partially connected to said ink jet recordable substrate.

49. The multilayer article of claim 38 wherein said magnetizable material is at least partially connected to said substantially nonporous material.

50. The multilayer article of claim 38 wherein said ink jet recordable substrate is a microporous substrate.

51. The multilayer article of claim 38 wherein said substantially nonporous material is polyvinyl chloride.

52. The multilayer article of claim 38 wherein said magnetizable material is at least partially coated with a substantially water-resistant coating composition.

53. The multilayer article of claim 52 wherein said substantially water-resistant coating composition is the coating composition of claim 1.

54. The multilayer article of claim 52 wherein at least one surface of said ink jet recordable substrate is at least partially coated with a substantially water-resistant coating composition.

- 86 -

55. The multilayer article of claim 52 wherein at least one surface of said substantially nonporous material is at least partially coated with a substantially water-resistant coating composition.

56. The multilayer article of claim 38 wherein at least one surface of said magnetizable material is at least partially coated with a friction reducing coating composition.

57. The multilayer article of claim 56 wherein said friction reducing coating composition further comprises at least one lubricant and at least one resin.

58. The multilayer article of claim 38 wherein said ink jet recordable substrate is at least partially coated with a friction reducing coating composition.

59. The multilayer article of claim 38 wherein said substantially nonporous material is at least partially coated with a friction reducing coating composition.

60. The multilayer article of claim 38 further comprising a release liner at least partially connected to at least one surface of said multilayer article.

61. A multilayer article comprising a microporous substrate at least partially connected to a first substantially nonporous material; said first substantially nonporous material at least partially connected to a second substantially nonporous material; said second substantially nonporous material at least partially connected to a third substantially nonporous material; said third substantially nonporous material comprising a magnetizable material.

62. A multilayer article comprising a magnetizable material at least partially connected to an adhesive material and said adhesive material at least partially connected to a substantially nonporous material.

63. A multilayer article comprising a magnetizable material at least partially connected to an adhesive

- 87 -

material and said adhesive material at least partially connected to an ink jet recordable material.

64. A multilayer article comprising a magnetizable material, an ink jet recordable substrate and a substantially nonporous material wherein said ink jet recordable substrate is at least partially coated with a substantially water-resistant coating composition, and at least one of said ink jet recordable substrate and substantially nonporous material is at least partially coated with a friction-reducing coating composition.

65. A multilayer article comprising an ink jet recordable substrate, at least one substantially nonporous material and a data transmittance/storage device.

66. The multilayer article of claim 65 wherein said data transmittance/storage device comprises a carrier material.

67. The multilayer article of claim 66 wherein said carrier material is polyvinylchloride.

68. The multilayer article of claim 65 wherein said data transmittance/storage device comprises a barrier material.

69. The multilayer article of claim 68 wherein said data transmittance/storage device can be at least partially connected to said barrier material using an adhesive material.

70. The multilayer article of claim 68 wherein at least one surface of said barrier material is at least partially coated with a coating composition selected from a substantially water-resistant coating composition, or a friction reducing coating composition or a combination thereof.

71. The multilayer article of claim 68 wherein said barrier material comprises a substantially nonporous material.

72. A multilayer article comprising a microporous substrate at least partially connected to a substantially nonporous material, said microporous substrate at least

- 88 -

partially coated with a substantially water-resistant coating composition, said coating composition comprising a stable dispersion of:

- (a) an aqueous polyurethane dispersion; and
- (b) a cationic nitrogen-containing polymeric dye fixative material at least partially dissolved in an aqueous medium.

73. The multilayer article of claim 72 wherein said microporous substrate comprises:

- (a) a polyolefin;
- (b) a particulate silica material; and
- (c) a porosity wherein the pores constitute at least 35 percent by volume of the microporous substrate.

74. The multilayer article of claim 73 wherein said polyolefin is chosen from polyethylene, polypropylene, and mixtures thereof.

75. The multilayer article of claim 74 wherein said polyethylene comprises an essentially linear high molecular weight polyethylene having an intrinsic viscosity of at least 10 deciliters/gram, and said polypropylene comprises an essentially linear high molecular weight polypropylene having an intrinsic viscosity of at least 5 deciliters/gram.

76. The multilayer article of claim 73 wherein said particulate silica material comprises precipitated silica.

77. The multilayer article of claim 72 wherein said aqueous polyurethane dispersion is chosen from aqueous dispersions of anionic polyurethanes, cationic polyurethanes, nonionic polyurethanes and mixtures thereof.

78. The multilayer article of claim 77 wherein said anionic polyurethane is chosen from aromatic polyether polyurethanes, aliphatic polyether polyurethanes, aromatic polyester polyurethanes, aliphatic polyester polyurethanes, aromatic polycaprolactam polyurethanes, aliphatic polycaprolactam polyurethanes, and mixtures thereof.

79. The multilayer article of claim 72 wherein said substantially nonporous material is chosen from substantially nonporous thermoplastic polymers, substantially nonporous metalized thermoplastic polymers, substantially nonporous thermoset polymers, substantially nonporous elastomerics, substantially nonporous metals and mixtures thereof.

80. A method for producing a multilayer article comprising the steps of:

- (a) providing a microporous substrate having a top surface and a bottom surface;
- (b) providing a substantially water-resistant coating composition comprising a stable dispersion of:
 - a. an aqueous polyurethane dispersion; and
 - b. a cationic nitrogen-containing polymeric dye fixative material at least partially dissolved in an aqueous medium;
- (c) at least partially applying said coating composition to at least one surface of said microporous substrate;
- (d) at least partially connecting said microporous substrate of (c) to a substantially nonporous material.

81. A substantially water-resistant ink jet recordable substrate coating composition comprising:

- a. an aqueous polyurethane dispersion;

- 90 -

- b. a cationic nitrogen-containing polymeric dye fixative compound; and
 - c. an acrylic polymer,
- wherein said coating composition has a pH of 7 or less.

82. The coating composition of claim 81 wherein said polyurethane dispersion is chosen from anionic polymers, cationic and nonionic polyurethanes dispersible in water.

83. The coating composition of claim 81 wherein said polyurethane dispersion comprises a polyisocyanate and a polyol.

84. The coating composition of claim 81 wherein said cationic nitrogen-containing polymeric dye fixative compound comprises polyamine and epichlorohydrin.

85. The coating composition of claim 81 wherein said acrylic polymer comprises a cationic acrylic polymer.

86. The coating composition of claim 85 wherein said cationic acrylic polymer is chosen from polyacrylates, polymethacrylates, polyacrylonitriles and polymers having monomer types selected from acrylonitrile, acrylic acid, acrylamide and mixtures thereof.

87. A method of preparing a substantially water-resistant ink jet recordable substrate coating composition comprising the step of mixing a nitrogen-containing polymeric dye fixative compound with an aqueous polyurethane dispersion and an acrylic polymer to produce a substantially homogeneous mixture having a pH of 7 or less.

- 91 -

88. A substantially water-resistant ink jet recordable substrate at least partially coated with a coating composition comprising:

- a. an aqueous polyurethane dispersion;
- b. an aqueous solution of a cationic nitrogen-containing polymeric dye fixative compound;
- and

- c. an acrylic polymer,

wherein said coating composition has a pH of 7 or less.

89. The ink jet recordable substrate of claim 88 further comprising bonding said substrate to at least one layer of a substantially nonporous material.