(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 962 330 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
08.12.1999 Bulletin 1999/49

(51) Int. Cl.[6]: **B41M 5/00**

(21) Application number: **99110775.6**

(22) Date of filing: **04.06.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **05.06.1998 US 88231 P**

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(54) An ink jet recording medium having an ink-receptive coating comprising two layers prepared from aqueous-based solutions

(57) This invention relates to an ink jet recording medium having an ink-receptive coating comprising two layers. The coating is prepared from aqueous-based solutions. The under layer comprises a blend of poly(2-ethyl-2-oxazoline) and hydrophilic, water-insoluble polyurethane, while the upper layer comprises a blend of polysaccharide and water-insoluble polymer. The coated ink jet recording media are capable of forming a high-quality, fast-drying printed image that is free of pigmented ink cracking.

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Description

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of United States provisional application 60/088,231 having a filing date of June 5, 1998.

BACKGROUND OF THE INVENTION

Field Of The Invention

[0002] The present invention relates to an ink jet recording medium having an ink-receptive coating comprising two layers. The coating is prepared from aqueous-based solutions. The under layer comprises a blend of poly(2-ethyl-2-oxazoline) and hydrophilic, water-insoluble polyurethane, and the upper layer comprises a blend of polysaccharide and water-insoluble polymer.

Brief Description Of The Related Art

[0003] Ink jet printing devices must be capable of recording multicolor images and text on media such as papers and films for many different applications. For example, ink jet recording media are used for overhead transparencies, engineering drawings, and large and small graphic art displays. Some ink jet recording media are coated with ink-receptive compositions containing water-soluble polymers. Traditionally, most inks used in ink jet printing devices consist of molecular dyes carried in an aqueous-based ink vehicle. By the term, "aqueous-based ink vehicle", it is meant a fluid containing a substantial amount of water. Water-miscible solvents and trace amounts of high-boiling solvents such as glycol or glycol ethers may also be present in the fluid. During imaging (i.e., printing), molecular dyes from the ink penetrate into the ink-receptive coating, leaving solvent to evaporate off the surface of the imaged media. Today, pigmented inks are replacing molecular dye-based inks. Pigmented-based inks have better light stability than molecular dye-based inks which is important for imaged media that are displayed outdoors. In addition, the optical density of black pigmented inks is greater than black molecular dye-based inks which is important for overhead transparency film products.

[0004] Pigmented inks comprise a pigmented colorant carried in an aqueous-based ink vehicle. Unlike molecular dyes, pigmented colorants generally bind to the surface of the recording medium. Since some ink jet recording media are coated with ink-receptive compositions containing water-soluble polymers, which are extremely water-absorptive, a problem may arise when pigmented inks are used on such media. During imaging, the pigmented colorants generally accumulate on the surface of such media, while the aqueous-based ink vehicle is absorbed, resulting in expansion of the ink-receptive coating. This expansion may cause pigmented ink cracks to appear in the final image.

[0005] Another problem with ink jet recording media is that the ink-receptive coating must have sufficient thickness to absorb the aqueous-based ink vehicle. As the thickness of the ink-receptive coating is increased, making it more water-absorptive and dimensionally-stable, the media tends to curl upwards along its edges. Previous attempts have been made at developing suitable ink-receptive coatings for ink jet media.

[0006] For example, Duan, U.S. Patent 4,781,978 discloses a substrate bearing an optically clear, non-cross linked coating formed from a blend comprising at least one polymer containing carbonylamido functional groups and at least one hydrophobic polymer substantially free of acidic functional groups. The coating is described as useful for promoting adhesion between the substrate and additional layers, increasing the hydrophilicity of the surface of the substrate, and increasing receptivity of the substrate for aqueous-based inks.

[0007] Edwards, U.S. Patent 4,956,230 discloses a transparent sheet for use with ink jet printers and pen plotters that utilize hydrophilic solvent-based inks. The sheet is described as comprising a transparent backing bearing on at least one major surface thereof a transparent coating formed of a blend of at least one hydrophilic polymer containing a carbonylamido functional group and at least one hydrophobic polymer substantially free of acidic functional groups, hydroxyl groups, >NH groups and-NH_2 groups.

[0008] Iqbal et at., U.S. Patent 4,935,307 discloses a hydrophilic polymer blend which provides improved durability and reduced curl when used as an image-receptive layer on graphic arts film. The blend comprises at least one water-absorbing, hydrophilic polymeric material, at least one hydrophobic polymeric material having acid functionality, and at least one polyethylene glycol

[0009] Mouri et al., U.S. Patent 4,642,247 discloses a recording medium fix recording with aqueous ink comprising an under layer and an upper layer. The upper layer is formed of substantially water-resistant resin and the under layer is more hydrophilic than upper layer.

[0010] Sargeant et al., U.S. Patent 5,700,582 discloses a polymer matrix coating used for ink jet recording media. The polymer matrix coating is described as having a glass transition temperature that is greater than or equal to about

120°C and less than or equal to 300°C, an integrity value of greater than or equal to about -20%, and a swellability of greater than or equal to about 50%. Poly(2-ethyl-2-oxazoline), cellulose ethers, and cellulose esters are described as examples of water-soluble components for the polymer matrix

[0011] It would be desirable to have an ink jet recording medium that could be imaged with aqueous-based pigmented inks to form a printed image having high resolution that is free of pigmented ink cracking, especially black pigmented ink cracking. There is also a need for a dimensionally-stable ink jet recording medium that remains flat and does not curl along its edges. The present invention provides such ink jet recording media.

SUMMARY OF THE INVENTION

[0012] The present invention relates to an ink jet recording medium comprising a substrate having an ink-receptive coating comprising two layers prepared from aqueous-based solutions. The under layer of the ink-receptive coating comprises a blend of poly(2-ethyl-2-oxazoline) and hydrophilic, water-insoluble polyurethane, while the upper layer comprises a blend of polysaccharide and water-insoluble polymer.

[0013] The hydrophilic, water-insoluble polyurethane may be, for example, a carboxylated, polyester-type, or polyether-type polyurethane, and mixtures thereof. The polysaccharide may be, for example, a water-soluble cellulose derivative dextran, chitosan, hyluronic acid, starch, or alginate, and mixtures thereof Preferably, the water-soluble cellulose derivative is hydroxypropylmethylcellulose. The water-insoluble polymer may be, for example, a poly(vinyl chloride), polyester, poly(vinylidene fluoride), an acrylate, or polyurethane, and mixtures thereof

[0014] Preferably, the poly(2-ethyl-2-oxazoline) comprises about 70 to about 90 % by weight, and the hydrophilic, water-insoluble polyurethane comprises about 10 to about 30 % by weight, based on the weight of the under layer of the coating.

[0015] Preferably, the polysaccharide comprises about 60 to about 90 % by weight, and the water-insoluble polymer comprises about 10 to about 40 % by weight based on the weight of the upper layer of the coating.

[0016] The ink-receptive coating may further contain particulate such as alumina, silica, poly(methyl methacrylate), or fluorinated polyethylene. The substrate is typically a polymeric film or paper, and the ink-receptive coating may be prepared by coating the substrate with an aqueous blend of poly(2-ethyl-2-oxazoline) and polyurethane and an aqueous blend of polysaccharide and water-insoluble polymer.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention relates to an ink jet recording medium comprising a substrate having a two-layered ink-receptive coating prepared from aqueous-based solutions.

[0018] The under layer of the ink-receptive coating comprises a blend of poly(2-ethyl-2-oxazoline) and polyurethane. (The under layer may also be referred to as the bottom or first layer.) Poly(2-ethyl-2-oxazoline) is a hydrophilic and water-soluble polymer; thus, it tends to swell upon exposure to the aqueous fluid in the pigmented ink during imaging and may absorb the aqueous fluid. In contrast, the polyurethane used in the ink-receptive coating of this invention is a hydrophilic, water-insoluble polymer. It has been found that this specific blend of poly(2-ethyl-2-oxazoline) and polyurethane is particularly effective in absorbing inks, while also providing dimensional stability to the media and substantially reducing image cracking and media curl. Suitable hydrophilic, water-insoluble polyurethanes include carboxylated polyurethanes, polyester-type polyurethanes, and polyether-type polyurethanes. The polyurethane may be in the form of a dispersion or emulsion. Sancure ®815, a carboxylated polyurethane available from B.F. Goodrich, is an example of a suitable polyurethane dispersion that can be used to prepare the under layer of the ink-receptive coating of this invention.

[0019] Preferably, the poly(2-ethyl-2-oxazoline) comprises about 70 to about 90 % by weight and the hydrophilic, water-insoluble polyurethane comprises about 10 to about 30 % by weight, based on the weight of the under layer of the ink-receptive coating.

[0020] The upper layer of the ink-receptive coating comprises a blend of polysaccharide and water-insoluble polymer(s). (The upper layer may also be referred to as the surface or second layer.) The pigmented colorants from the aqueous pigmented inks tend to bind to the surface layer, while the aqueous-based ink vehicle substantially permeates through the surface layer and is absorbed by the bottom layer. This upper layer is particularly effective in reducing the amount of pigmented ink cracking that may appear on imaged media as discussed above.

[0021] Suitable polysaccharides include those selected from the group consisting of water-soluble cellulose derivatives, dextran, chitosan, hyluronic acid, starch, and alginates, and mixtures thereof. Examples of suitable water-soluble cellulose derivatives include methylcellulose, hydroxymethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, carboxymethylcellulose, and hydroxyethylcellulose. Methocel ®K35, a hydroxypropyl methylcellulose available from Dow Chemical, is an example of a suitable cellulose derivative that can be used to prepare the second layer of the ink-receptive coating of this invention.

[0022] Suitable water-insoluble polymers that can be blended with the polysaccharide include poly(vinyl chloride), polyesters, poly(vinylidene fluoride), acrylates such as methyl methacrylate, styrene-acrylonitrile polymers, polyurethanes, polysulfones, butadienes, 2-hydroxyethyl acrylate, ethyl acrylate, N-hydroxyethyl acrylamide, N-hydroxymethylacrylamide, and polycarbonates. Preferably, a water-insoluble polyurethane is blended with the polysaccharide and used in the upper layer.

[0023] Preferably, the polysaccharide comprises about 60 to about 90 % by weight, and the water-insoluble polymer comprises about 10 to about 40 % by weight, based on the weight of the upper layer of the ink-receptive coating.

[0024] The ink jet recording media of this invention can be made using any suitable substrate such as a polymeric film or paper. Examples of suitable polymeric films include films made of polymers selected from the group consisting of polyesters, cellulose esters, polyimides, polystyrenes, polyolefins, poly(vinyl acetates), polycarbonates, and fluoropolymers, and mixtures thereof Examples of suitable papers included plain papers, clay-coated papers, and resin-coated papers. Polyester films are particularly preferred film substrates. Clay-coated and polyethylene-coated papers are particularly preferred paper substrates. The thickness of the base substrate may vary, but is typically in the range of about 1 mil to about 10 mils, and most typically in the range of about 3 mils to about 5 mils.

[0025] The base substrate may be treated with a conventional adhesion promoting layer on its imaging surface as is known in the art. If desired, the non-imaging surface of the base substrate may have a backing material placed thereon in order to reduce electrostatic charge and sheet-to-sheet sticking. The backing maybe a polymeric coating, polymeric film, or paper.

[0026] Various additives may also be employed in one or both layers of the ink-receptive coating. These additives include surface active agents that control the wetting or spreading action of the coating solutions, antistatic agents, suspending agents, acidic compounds to control the pH of the coating, optical brighteners, and UV blockers/stabilizers. Particulate may be used to provide anti-blocking properties to the ink jet recording medium. Preferably, the particulate has a narrow particle size distribution with an average particle size of about 0.3 micrometers to about 40 micrometers and more preferably about 0.5 to about 22 micrometers. Examples of suitable inorganic particles include silica, alumina, kaolin, glass beads, calcium carbonate, and titanium dioxide. Examples of suitable organic particles include polyolefins, polystyrene, starch, poly(methyl methacrylate), and poly(tetrafluoroethylene).

[0027] The under layer of the ink-receptive coating may be prepared by dissolving poly(2-ethyl-2-oxazoline) in water to from an aqueous-based solution, and then adding polyurethane, in the form of a dispersion, to the solution. By the term, "aqueous-based" solution, it is meant a solution prepared using water as the major solvent. Water-miscible solvents, wetting agents, surfactants, anti-foam agents, film-forming agents, particulate, and other additives as described above may be present in minor amounts. The under layer is then coated onto the surface of the substrate and typically dried.

[0028] The upper layer of the ink-receptive coating maybe prepared by dissolving polysaccharide in water to from an aqueous-based solution, and then adding the water-insoluble polymer to the solution. The upper layer is then coated onto the under layer and dried.

[0029] Conventional coating and drying methods may be employed including roller coating, blade coating, wire bar coating, dip coating, extrusion coating, air knife coating, curtain coating, slide coating, doctor coating, gravure coating, or slot-die coating. The coating layers may be dried in an oven.

[0030] In a preferred embodiment, the under layer of the ink-receptive coating is applied to the substrate at a thickness of about 7 to about 40 grams per-square meter, while the upper layer is applied at a thickness of about 1 gram per square meter to about 5 grams per square meter.

[0031] It has been found that the ink-receptive coating of this invention is capable of forming a fast-drying printed image having high resolution that is essentially free of pigmented ink cracking. The ink jet recording media of this invention, having this ink-receptive coating, are dimensionally stable and do not exhibit substantial curl along their edges.

[0032] The invention is further illustrated by the following examples using the below test methods, but these examples should not be construed as limiting the scope of the invention.

Test Methods

Drying Time

[0033] The ink jet recording media were imaged with a Hewlett-Packard HP DeskJet ® 850C printer, and the amount of time necessary for an imaged medium to dry was determined. After imaging, a plain paper was placed on the imaged surface of the medium and a six (6) pound roller was rolled over the paper. The amount of ink transfer from the medium to the plain paper was observed and the dry time was calculated. Dry time is calculated based on the point at which no ink transfer from the medium to the paper is observed.

Image Density

[0034] The ink jet recording media were imaged with a HP DeskJet ®850C printer, and the ink density of the imaged medium was determined. The black pigment ink density (KOD) of the imaged surface was measured on a densitometer (MacbethTD904 available from Macbeth Process Measurements,Newburgh, NY) following the manufacturer's standard recommendations. Samples having high ink density values exhibit images having better quality and higher resolution than samples having low ink density values. Significant black pigmented ink cracking on the image is observed when black KOD is less than 1.8.

Image Coalescence

[0035] The ink jet recording media were imaged with a Hewlett-Packard HP DeskJet ®850C printer, and the image coalescence of the imaged medium was observed. The imaged media were visually inspected and assigned a value on the scale of one (1) to ten (10), with 10 representing excellent image quality and resolution and 1 representing poor image quality and resolution.

EXAMPLES

Example 1

[0036] A polyester film was coated with an ink-receptive coating comprising a bottom layer and surface layer. The below-described bottom layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described surface layer formulation was then applied to the bottom layer using a metering rod and dried at 130°C for 5 minutes.

Bottom layer	
Aquazol AI[1]	14.70 parts
Sancure 815[2]	4.10 parts
Classified Soken MR20G[3]	0.15 parts
Water	81.10 parts
Upper layer	
Methocel K35[4]	3.90 parts
Sancure 815	1.00 parts
Water	95.10 parts

[1] poly(2-ethyl-2-oxazoline), available from Polymer Chemistry Innovations, Inc.
[2] polyurethane dispersion, available from B.F. Goodrich.
[3] poly(methyl methacrylate) beads, available from Esprit Chemical Company
[4] hydroxypropyl methylcellulose available from Dow Chemicals

[0037] The coated ink jet recording medium was imaged as described above, resulting in high quality images having good resolution that were essentially free from pigmented ink cracks. The imaged medium did not exhibit any substantial curl. The imaged medium was tested for different properties and the results are reported below in Table 1.

Example 2

[0038] A polyester film was coated with an ink-receptive coating comprising an under layer and upper layer. The below-described under layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described upper layer formulation was then applied to the under layer using a metering rod and dried at 130°C for 5 minutes.

Under layer:	
Aquazol AI	14.90 parts
Sancure 815	3.60parts
Classified Soken MR20G	0.15 parts
Water	81.40 parts
Upper layer:	
Methocel K35	3.90 parts
Sancure 815	1.00 parts
Water	95.10 parts

[0039] The coated ink jet recording medium was imaged as described above, resulting in high quality images having good resolution that were essentially free from pigmented ink cracks. The imaged medium did not exhibit any substantial curl. The imaged medium was tested for different properties and the results are reported below in Table 1.

<u>Example 3</u>

[0040] A polyester film was coated with an ink-receptive coating comprising a bottom layer and surface layer. The below-described bottom layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described surface layer formulation was then applied to the bottom layer using a metering rod and dried at 130°C for 5 minutes.

Bottom layer:	
Aquazol AI	15.50 parts
Sancure 815	2.48 parts
Classified Soken MR20G	0.15 parts
Water	81.87 parts
Surface layer:	
Methocel K35	1.39 parts
Methocel A4M[5]	0.60 parts
Sancure 815	0.99 parts
MEK[6]	2.86 parts
Water	94.16 parts

[5] hydroxypropyl methylcellulose available from Dow Chemicals.
[6] methyl ethyl ketone.

[0041] The coated ink jet recording medium was imaged as described above; resulting in high quality images having good resolution that were essentially free from pigmented ink cracks. The imaged medium did not exhibit any substantial curl. The imaged medium was tested for different properties and the results are reported below in Table 1.

Example 4

[0042] A polyester film was coated with an ink-receptive coating comprising a bottom layer and surface layer. The below-described bottom layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described surface layer formulation was then applied to the bottom layer using a metering rod and dried at 130°C for 5 minutes.

Bottom layer	
Aquazol Al	14.45 parts
Witcobond W234[7]	4.05 parts
Soken MR28G[8]	0.14 parts
Water	81.87 parts
Surface layer:	
Methocel A4M	1.00 parts
Eastek 1000[9]	0.99 parts
MEK	2.86 parts
Water	95.15 Parts

[7]polyurethane dispersion, available from Witco.
[8]poly(methyl methacrylate) beads, available from Espirit Chemical Company.
[9]polyester dispersion, available from Eastman Chemical Company.

[0043] The coated ink jet recording medium was imaged on different printers as described above, resulting in high quality images having good resolution that were essentially free from pigmented ink cracks. The imaged medium did not exhibit any substantial curl. The imaged medium was tested for different properties and the results are reported below in Table 1.

Example 5

[0044] A polyester film was coated with an ink-receptive coating comprising a bottom layer and surface layer. The below-described bottom layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described surface layer formulation was then applied to the bottom layer using a metering rod and dried at 130°C for 5 minutes.

Bottom layer	
Aquazol Al	14.70 parts
Sancure 815	4.10 parts
Soken MR20G	0.14 parts
Water	81.87 parts
Surface layer:	
Methocel A4M	0.66 parts
QP 52,000[10]	0.33 parts
Eastek 1000	0.16 parts
Water	98.85 parts

[10]Hydroxy ethyl cellulose, available from Union Carbide.

[0045] The coated ink jet recording medium was imaged as described above, resulting in high quality images having good resolution that were essentially free from pigmented ink cracks. The imaged medium did not exhibit any substantial curl. The imaged medium was tested for different properties and the results are reported below in Table 1.

<u>Comparative Example A</u>

[0046] A polyester film was coated with an ink-receptive coating comprising an under layer and an upper layer. The below-described under layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described upper layer formulation was then applied to the inter-layer using a metering rod and dried at 130°C for 5 minutes.

Under layer:	
Aquazol Al	14.70 parts
Sancure 815	4.10 parts
Classified Soken MR20G	0.15 parts
Water	81.10parts
Upper layer:	
Methocel K35	3.90 parts
Water	96.10 parts

[0047] The coated ink jet recording medium was imaged as described above, resulting in low quality images having poor resolution, and pigmented ink cracks were observed. The imaged medium was tested for different properties and the results are reported below in Table 1.

<u>Comparative Example B</u>

[0048] A polyester film was coated with an ink-receptive coating comprising an under layer and an upper layer. The below-described under layer formulation was applied to the film using a metering rod and dried in an oven at 130°C for 5 minutes. The below-described upper layer formulation was then applied to the bottom layer using a metering rod and dried at 130°C for 5 minutes.

Under layer:	
Aquazol Al	14.70 parts
Soken MR20G	0.15 parts
Water	85.20 parts
Upper layer:	
Methocel A4M	0.66 parts
QP 52,000	0.33 parts
Eastek 1000	0.16 parts
Water	98.85 parts

[0049] The coated ink jet recording medium was imaged as described above, resulting in low quality images having poor resolution, and pigmented ink cracks were observed. The imaged medium was tested for different properties and the results are reported below in Table 1.

TABLE 1

IMAGE PROPERTIES OF THE MEDIA			
Sample	KOD	Dry Time (seconds)	Coalescence
Example 1	1.9	120	9
Example 2	2.1	100	9
Example 3	2.4	105	9
Example 4	2.2	120	8
Example 5	2.1	110	9
Example 6	2.9	105	9
Comparative Example A	1.2	125	6
Comparative Example B	0.9	140	6

[0050] As shown in above Table 1, the ink jet recording media having an ink-receptive coating in accordance with this invention provide a high quality printed image having high resolution; high black KOD, indicating no pigmented ink cracking; and good ink coalescence. Further, the drying time for images on the media of this invention is relatively short. In contrast, ink jet recording media that do not have an ink-receptive coating in accordance with this invention, provide a lower quality printed image having poor resolution, low black KOD, indicating pigmented ink image cracking; and ink coalescence. The drying time for images on these media is relatively long.

Claims

1. An ink jet recording medium comprising a substrate having an ink-receptive coating comprising an under and upper layer, said under layer comprising a blend of poly(2-ethyl-2-oxazoline) and hydrophilic, water-insoluble polyurethane and said upper layer comprising a blend of polysaccharide and water-insoluble polymer.

2. The ink jet recording medium of claim 1, wherein the hydrophilic, water-insoluble polyurethane is selected from the group consisting of carboxylated polyurethanes, polyester-type polyurethanes, and polyether-type polyurethanes, and mixtures thereof.

3. The ink jet recording medium of claim 1, wherein the polysaccharide is selected from the group consisting of water-soluble cellulose derivatives, dextran, chitosan, hyluronic acid, starch, and alginates, and mixtures thereof.

4. The ink jet recording medium of claim 3, wherein the water-soluble cellulose derivative is hydroxypropylmethylcellulose.

5. The ink jet recording medium of claim 1, wherein the water-insoluble polymer is selected from the group consisting of poly(vinyl chloride), polyesters, poly(vinylidene fluoride), acrylates, and polyurethanes, and mixtures thereof.

6. The ink jet recording medium of claim 1, wherein the poly(2-ethyl-2-oxazoline) comprises about 70 to about 90 % by weight, and the hydrophilic, water-insoluble polyurethane comprises about 10 to about 30 % by weight, based on the weight of the under layer.

7. The ink jet recording medium of claim 1, wherein the polysaccharide comprises about 60 to about 90 % by weight, and the water-insoluble polymer comprises about 10 to about 40 % by weight, based on the weight of the upper layer.

8. The ink jet recording medium of claim 1, wherein the ink-receptive coating further comprises particulate selected from the group consisting of alumina, silica, poly(methyl methacrylate), polystyrene, starch, and fluorinated polyethylene.

9. The ink jet recording medium of claim 1, wherein the substrate is a polymeric film or paper.

10. The ink jet recording medium of claim 1, wherein the ink-receptive coating is prepared by coating the substrate with an aqueous blend of poly(2-ethyl-2-oxazoline) and hydrophilic, water-insoluble polyurethane and an aqueous blend of polysaccharide and water-insoluble polymer..