IM-0915

TITLE

INK JET RECORDING SHEET

FIELD OF THE INVENTION

This invention relates to a recording sheet for use in ink jet printing. More particularly, this invention relates to recording medium having improved coatability, drying characteristics, and print quality. In a preferred embodiment, the invention provides a reactive ink jet recording sheet having improved durability, water-fastness and smear resistance.

BACKGROUND OF THE INVENTION

Ink jet printing is a non-impact method for recording information in response to an electronic signal, such as that generated by a computer. In the printer the electronic signal produces droplets of ink that are deposited on a substrate such as paper. Ink jet printers have found broad commercial acceptance due to their rapid printing speeds, relatively quiet operation, graphic capability and low cost.

In current ink jet printing applications, several inks (typically black, cyan, magenta and yellow) are used to print textual and graphic information on a printing medium, typically ordinary paper. The inks primarily are composed of water, a colorant that may be a dye or pigment dispersion, generally contain a polyhydric alcohol to prevent nozzle clogging, and may contain various adjuvants. Such inks and ordinary paper are well suited for desk-top publishing, as currently practiced, wherein only a small portion of the paper receives printed text and graphic information.

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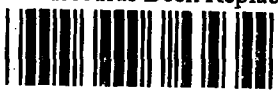


It also is desired to reproduce high quality colored pictoral information (such as photographs and the like) using ink jet technologies for applications such as commercial printing and desk-top publishing. In these applications, however, the printing medium will receive substantially more of the black and colored inks to accurately reproduce the various hues, tints, and colors contained in a typical colored picture. For example, the printing medium will be expected to receive up to 200% or more coverage in conventional commercial printing.

Ordinary paperstock is not suitable for such high quality applications for a number of reasons. Water disrupts the paper structure, causing "cockle" that affects appearance of the paper and, in extreme cases, may actually cause the paper to distort to the extent that it contacts the ink jet pen, disrupting the printing process. Also, the paper may not absorb water sufficiently quickly to achieve the desired printing speed, or may cause flooding of the paper surface, which adversely affects image quality. Moreover, wicking of ink into the paper may cause paper to "show through" into the printed image, detracting from image quality. There also is a need for the printed text and pictures to be more robust; e.g., exhibit better handleability, water fastness, and smear resistance. Accordingly, there is a need for improved media for ink jet printing in general, and particularly for applications of ink jet printing technologies to commercial printing and to reproduction of pictorial information.

Various coated recording media have been proposed in the patent literature for use with ink jet printers. For example, DE 3 016 766 discloses an ink jet recording sheet having a water-soluble polymer layer

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and JP 63 242,585 discloses a recording material in which the ink receptive layer is formed by a hydrophilic or water-soluble polymer.

U.S. 4,503,111 discloses a recording medium having a surface coated with polyvinylpyrrolidone and a compatible matrix-forming hydrophilic polymer, such as gelatin or polyvinyl alcohol. Inked images applied to such coatings are relatively slow to dry, however, and exhibit poor waterfastness and poor handleabilty due to the tackiness of the surface coating.

Recording media containing resin blends are disclosed in U.S. 4,857,386, which provides an ink absorbent resin layer of polyvinyl pyrrolidone polymer and an acrylic or methacrylic polymer. Water absorbancy is thereby improved, but the coatings still dry too slowly and exhibit some tackiness.

U.S. 4,686,118 discloses an ink receiving layer comprising a mixture of a polymer capable of forming intermolecular hydrogen bonds and a polymer incapable of forming intermolecular hydrogen bonds. An ink permeable layer is also provided which contains polymers formed from acrylic acid ester, polymers formed from vinyl acetate, vinyl chloride or other hydrophilic vinyl monomers and cellulose derivatives. Although this two layer structure provides excellent durability, it has disadvantages in that coatability is more difficult and the second layer provides one additional interface for adhesive failure.

JP 61 193,879 discloses a recording sheet consisting of a film containing a mixture of polyvinyl pyrrolidone and a water-soluble cellulose on a transparent support. These coatings have a tendency to be too water-soluble and not dry well.

Consequently, there continues to be a need for improved media that will enable ink jet printing to be

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used in high quality applications, such as commercial printing.

SUMMARY OF THE INVENTION

The present invention provides an improved recording sheet having excellent coatability, and water-fastness, which exhibits fast drying time and provides images having high print quality in demanding applications wherein high levels of inks are applied to the sheet. Accordingly, the invention provides a recording sheet that bears a coating containing:

(a) 15 to 80 % by weight of at least one water-soluble vinyl polymer;

(b) 5 to 70 % by weight of at least one acrylic or methacrylic polymer having a number average molecular weight of at least 10,000; and

(c) 5 to 50 % by weight of at least one water-soluble cellulose compound;

wherein the % by weight is based on the weight of the total composition.

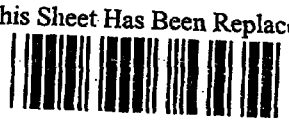
In a preferred embodiment, the coating has superior durability by including a reactive species that hardens the coating, after printing, through exposure to heat, light, or other activating energy.

These ink jet recording sheets are particularly useful in commercial printing applications.

DETAILED DESCRIPTION OF THE INVENTION

The coating composition contains a blend of (a) a water-soluble vinyl polymer, (b) an acrylic or methacrylic polymer having a number average molecular weight of at least 10,000, and (c) a water-soluble cellulose compound. The composition provides superior performance compared to compositions containing a

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single component, or blends of only two components. Without the acrylic or methacrylic polymer, the composition is too water receptive, dries poorly, has poor water fastness and handleability. Drying is improved, and tackiness of the coating is decreased, through the presence of the water-soluble cellulose compound. The water-soluble vinyl polymer improves drying, print quality, and coatability. Optionally, the composition may contain fillers, additives, and a "reactive species" as described below.

Water-soluble Vinyl Polymer

The vinyl polymers that are selected in practicing the invention are water-soluble. Some suitable water-soluble vinyl polymers include polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl alcohol copolymers such as poly(vinyl alcohol-co-vinyl acetate) commonly known as partially hydrolyzed poly(vinyl alcohol), vinyl pyrrolidone copolymers such as poly(vinyl pyrrolidone-co-vinyl acetate), polyvinylpyridinium halide, polyvinylmethylethers, and blends thereof. The vinyl polymer may have molecular weight in the range of 10,000 to 1,000,000. Vinyl polymers having molecular weights in excess of about 100,000 are generally preferred.

The water-soluble vinyl polymers may be present in the amount of 15 to 80 % by weight, preferably 50 to 70 % by weight, based the weight of the total coating composition.

Acrylic Or Methacrylic Polymer

The acrylic or methacrylic polymer component of the coating has a molecular weight of at least 10,000, and may be a homopolymer, a copolymer, or mixtures thereof. Suitable monomeric components of such

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polymers include acrylic acid, methacrylic acid, lower alkyl of 1 to 6 carbon atoms acrylate esters, lower alkyl of 1 to 6 carbon atoms methacrylate esters, styrene, dialkylamino acrylates and dialkylamino methacrylates. A particularly suitable ink absorbent resin contains free carboxylic acid groups, and has an acid number (mg KOH per g) not exceeding 150, and preferably of from 20 to 120; for example, a copolymer of methacrylic acid and methylmethacrylate with an acid number (mg KOH per g) of from about 60 to 100, particularly about 80. In one embodiment of the invention the acrylic or methacrylic polymer component contains hydroxylic functionality. The acrylic or methacrylic polymer may be a super absorbent polymer where the acrylic or methacrylic polymer is modified to the salt form of the carboxylates or sulfonates. An example of a super absorbent polymer is Abcote® 56220 sold by Morton Company.

Representative useful acrylic or methacrylic polymers include methyl methacrylate(37%)/ethyl acrylate(56%)/acrylic acid(7%) terpolymer, acid no. 76-85, molecular weight 260,000; methyl methacrylate(61.75%)/ethyl acrylate(25.75%)/acrylic acid(12.5%) terpolymer, acid no. 100, molecular weight 200,000; etc. An acrylic polymer containing alkylaminoethylmethacrylate, such as a copolymer of butyl methacrylate/dimethylaminoethyl methacrylate, (80/20), average molecular weight 11,000, may be used to advantage.

The acrylic or methacrylic polymer may be present in the amount of 5 to 70 % by weight, preferably 10 to 30 % by weight based on the total composition.

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Water-soluble Cellulose Compound

The water-soluble cellulose compound is a compound on which water solubility is conferred by replacement of -OH groups in the cellulose. The water-soluble cellulose compound may be an alkyl cellulose, cyanoalkyl cellulose, carboxalkyl cellulose, carboxyalkyhydroxyalkyl cellulose, hydroxyalkyl cellulose, hydroxyalkylmethyl cellulose wherein the alkyl is 1 to 4 carbon atoms, and cellulose esters which are made soluble by making the salt of the acid or hydroxy groups, eg. partial esters. Representative water-soluble cellulose compounds include methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and methylhydroxypropyl cellulose.

The water-soluble cellulose compound may be present in the amount of 5 to 50 % by weight, preferably 10 to 30 % by weight based on the total composition.

Fillers

The filler component, if used, is generally an inorganic pigment such as silica, various silicates, zeolites, calcined kaolins, diatomaceous earths, barium sulfate, aluminum hydroxides, calcium carbonate, or the like.

Additives

In addition to the primary ingredients the coatable film layer can contain other additives. For example, surfactants, plasticizers, humectants, UV absorbers, polymeric dispersants, difoamers, mold inhibitors, antioxidants, latex, dye mordants and optical brighteners may be included.

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Reactive species

The coating preferably contains at least one "reactive species" that improves durability, water-fastness, and smear-resistance of non-imaged as well as imaged areas of the printed medium upon exposure to an external energy source after the printing operation. The reactive species causes reaction of components in the coating and/or applied ink upon exposure to actinic radiation (preferably UV light), heat, or chemicals to cause the coating to become more durable and less receptive to water.

The reactive species may contain reactive acid groups, base groups, epoxy groups, styryl-pyridinium groups, styryl-pyrollium groups, dimethylmaleimide groups, cinnamic groups, unsaturated acrylic groups, and bis-azides that react with other groups present in the coating and/or in the ink. Catalysts may be included to initiate or accelerate reactions, provided that the catalyst does not prematurely initiate the reaction during the printing operation. UV initiators may be employed to advantage to generate the reactive species, such as free radicals or strong acids, for particular applications. Heat may be used to produce the reactive species; for example, epoxy groups may require heat to activate crosslinking. Reactive species may be used in combination with multivalent metal salts such as calcium, magnesium, zinc and aluminum to generate a chemical reaction with the coating components.

Derivatives of water-soluble polymers, such as polyvinyl alcohol, having pendant photocrosslinkable groups may be used to advantage in the coatable film layer. On exposure these groups react to form crosslinks between different polymer chains. Such photo-crosslinkable polymers are described in A. Reiser,

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Photoreactive Polymers: The Science and Technology of Resists, Wiley, New York, 1989, pp 24-32. Typical photocrosslinkable groups are the cinnamyl, chalcone, alpha-phenylmaleimide, N-alkyl styrylpyridinium, and N-alkyl styrylquinolinium groups.

Derivatives of polyvinyl alcohol having photocrosslinkable groups are preferred. Preferred polyvinyl alcohol derivatives have N-alkyl styrylpyridinium or N-alkyl styrylquinolinium groups. Such polymers are described in K. Ichimura and S. Wantanabe, J. Polym. Sci., Polym. Lett. Ed., 18, 613 (1980) and 20, 1411, 1419 (1982) as well as in Ichimura, U.S. Patents: 4,272,620, 4,287,335, 4,339,524, 4,564,580 and 4,777,114.

Substituted hydrophilic polyvinyl alcohol polymers typically are prepared by derivatization of saponified polyvinyl acetate with the appropriate photo-crosslinking group. It is desirable for the polyvinyl acetate to be at least 70% hydrolyzed. Typically 88% saponified polyvinyl acetate is used, but polyvinyl acetate which is more or less highly saponified can be used. The photocrosslinkable group can be attached to the polyvinyl alcohol by any appropriate chemical linkage, such as an ester, ether, or acetal linkage. The acetal linkage is preferred. Typically, 0.5-10 mol% photocrosslinkable groups, preferably 1-4 mol%, are present. The degree of polymerization of the polyvinyl alcohol (i.e., the number of monomer units in the polymer chain) is advantageously in the range of 400 to 3,000. When the polymerization degree is too low, the exposure time required for loss of hydrophilic character is lengthened. When the polymerization degree is too large, the viscosity of solutions containing the polymer becomes so large that they are difficult to prepare and handle.

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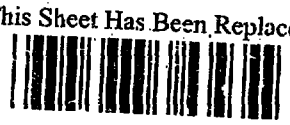
Styrylpyridinium or styrylquinolinium acrylates or methacrylates which may be used as the acrylate or methacrylate polymer are prepared as described in U.S. 4,272,620 using hydroxy containing acrylates or methacrylates instead of polyvinyl alcohol.

Another useful class of polyfunctional photoactivatable crosslinking agents are bis-azides. These compounds typically are aromatic bis-azides substituted with one or more ionic groups, such as sulfonate, carboxylate, sulfate, etc., to increase water solubility. Representative bis-azides are sodium 4,4'-diazidostilbene-2,2'-disulfonate, sodium 4,4'-diazidobenzalacetophenone-2-sulfonate, and sodium 4,4'-diazidostilbene-alpha-carboxylate. A preferred bis-azide is sodium 4,4'-diazidostilbene-2,2'-disulfonate. As will be apparent to those skilled in the art, equivalent results may be obtained from the use of bis-azides that contain other cations in place of sodium, such as potassium, ammonium, and substituted ammonium (e.g., ethyl ammonium, tetramethyl ammonium, etc.).

Loss of hydrophilic character is generally achieved by photoinitiated polymerization and/or crosslinking reactions. The resulting change in physical properties of the compounds present, particularly the increase in molecular weight and/or network formation, changes the hydrophilic character of the coating and/or the ink jet ink applied to it.

The amount of reactive species included in the coating composition will vary with the particular components of the composition, and the mechanism of activation, and can readily be determined by routine experimentation.

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SUPPORT

The support (i.e., substrate) may be any of those commonly used in printing. For ink jet ink applications in particular, cellulose and non-cellulose type substrates may be used to advantage, with porous cellulose type substrates, such as paper, being preferred. If sized, the degree of sizing for the substrate can be from 1 second to 1000 seconds as measured by the Hercules size test (HST), as described in TAPPI standards T530 PM-83. The substrate is chosen so its HST value is compatible with the volume and composition of the ink drop in the printer to be used. The preferred HST is in the range of 200 to 500 seconds, most preferably 350 to 400 seconds. Some useful papers are copier grade paper, 100% bleached kraft composed of a blend of hard and soft wood, 100% wood free cotton vellum, and wood containing paper made translucent either by pulp beating or with additives. A preferred paper is Gilbert Bond paper (25% cotton) designated style 1057, manufactured by Mead Company, Dayton, OH. Standard resin coated papers used in the photographic industry such as polyclad papers, preferably polyethylene clad papers, also may be selected to advantage.

Some illustrative examples of support for ink jet transparencies, which are non-porous and usually have a thickness of about 50 to 125 microns (preferably from about 100 to about 125 microns), include polyester films such as Mylar® flexible film, commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE; Melinex® film, commercially available from Imperial Chemicals, Inc.; Celanar® film, commercially available from Celanese Corp.; polycarbonates such as Lexan® sheet film, commercially available from The General Electric Company, Fairfield, CT; polysulfones, cellulose triacetate; polyvinylchlorides; and the like. Mylar®

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polyester film is preferred because of its availability and low cost. Coated transparent films, such as gel subbed polyester films, or polyester films with white opaque coatings on them used as proofing receptors, are also useful in practicing the invention.

Other substrates, such as cardboard or fabrics, may be selected for specialty applications.

The surface coating is applied to the sheet support surface at a dry coating weight of greater than 40 mg/dM^2, preferably 90-150 mg/dM^2 using conventional coating methods. Suitable coating methods include, for example, conventional roller coating or knife coating methods, trailing blade, and the like.

EXAMPLES

The invention will be further illustrated by, but not limited to, the following examples.

Example 1:

Solutions were prepared as follows:

Methacrylic Polymer Solution:

12 grams of methyl methacrylate(61.75%)/ethyl acrylate(25.75%)/acrylic acid(12.5%) terpolymer, acid no. 100, molecular weight 200,000, Tg = 70°C, were added to 150 grams water and 12 grams of 12M ammonium hydroxide to dissolve the polymer. An additional 200 grams of water were then added to give a 6% solution.

Cellulose Compound Solution:

Culminal® MHPC-25 (Aqualon, Wilmington, De) was slurried with 6 times its weight in water at 50-60°C. Cold water was then added to give a 5% solution.

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Vinyl Polymer Solution:

PVP K-30 (International Specialty Polymers, Wayne, N.J.) was dissolved in cold water to give a 6% solution.

Four coatable layers were prepared as follows:

The solutions prepared as described above were then blended in the ratios of solids given in Table 1 and coated with a #50 wire-wound rod on gel subbed 0.01 cm thick polyester base and dried.

TABLE 1

INGREDIENT	SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D (Control)
Methacrylic Polymer Solution	20	33	33	67
Vinyl Polymer Solution	60	33	17	0
Cellulose Compound Solution	20	33	50	33

Samples A-D were printed with a Stork Intelligence ink jet printer, Stork Corporation, Bedford, MA, with the results given in Table 2. All coatings had good coating quality with a non-tacky surface. Inks printed as round dots without splatter.

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TABLE 2

SAMPLE	ABSORBANCY	COMMENTS
A	good	good image
B	good	Some cracking in solid areas
C	fair	Cracking in solid areas
D	poor	Inks not dry after 24 hours

Example 2:

Coatings were made as described in Example 1 with the following exception: the solutions prepared as described above were then blended in the ratios of solids given in Table 3 and some samples were made with PVP K-60.

TABLE 3

SAMPLE	Methacrylic Polymer Solution	Vinyl Polymer Solution	Cellulose Compound Solution	Coating Weight
A	20	60	20	62
B[1]	0	80	20	68
C[1]	0	60	40	56
D*	20	60	20	83
E*[1]	0	80	20	76
F*[1]	0	60	40	69

* PVP K-60 solution was used in place of PVP-30

1 Control samples

Prints were made on the Stork Intelligence proofer and results are given in Table 4 below.

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TABLE 4

SAMPLE	COMMENTS
A	Somewhat slow dry. Puddles in areas of high ink coverage
B	Does not dry
C	Very slow dry. Puddles in areas of high ink coverage
D	Dries well. Puddling in areas of high ink coverage
E	Very poor drying
F	Poor drying. Break up in solid areas

Example 3:(Control)

Coatings were made as described in Example 1 with the following exception:no MHPC was added. Syloid® 72 silica, manufactured by Davision Chemical Division,W. R. Grace Corp., Baltimore, MD, was added as a matting agent. Formulations are given in Table 5.

TABLE 5

SAMPLE	6% Solution of Methacrylic Polymer (gms)	6% Solution of Vinyl Polymer (gms)	Syloid® 72 silica (gms)
A	6	23.75	0.25
B	6	23.50	0.50
C	6	23.25	0.75
D	6	23.00	1.00
E	6	22.50	1.50
F	6	22.00	2.00
G	6	21.00	3.00

The gloss was measured for each sample with a 75 degree gloss meter and samples were printed to test for absorbancy. Results are provided in Table 6.

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TABLE 6

SAMPLE	ABSORBANCY	GLOSS (%)
A	fair	30
B	poor	10
C	poor	5
D	poor	3
E	fair	2
F	good	2
G	good	2

At low silica loading without addition of MHPC, the coatings did not have good water absorbancy.

Example 4:

Example 1 is repeated with the following exception: polyvinyl alcohol (PVA) was used in place of PVP K-30. The PVA has a viscosity of 28-32 as a 4% solution, and a mole % degree of hydrolysis of 99 to 99.8. The solution is made as described in Example 1 of U.S. 5,141,797.

Example 5:

Example 1 is repeated with the following exception: styrylpyridinium acrylate is used as the acrylate polymer. It is prepared by reacting styrylpyridinium aldehyde with a copolymer of methyl methacrylate/hydroxyethyl methacrylate (60/40), average molecular weight of 12,000, as described in U.S. 4,272,620. After printing with an ink jet ink prepared as described in U.S. 5, 085,698, the resulting printed recording sheet is UV cured in a Cyrel® 1215 exposure unit (E.I. duPont de Nemours and Company, Wilmington, De), outfitted with high intensity UV flucrescent tubes

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with λmax = 353nm, at a distance of 3.81 cm from the recording sheet surface for a 2 minute exposure. The resulting image is expected to show much improvement in durability when compared to a sample that has not been UV cured.

Example 6:

Example 1 is repeated with the following exceptions: SPP 11-KM which is polyvinyl alcohol acetalized with N-methyl-4-(p-formystyryl)pyridinium methosulfate; Toyo Gosei Kogyo Company, Ltd., Ichikawa City, Chiba Pref., Japan is used as the vinyl polymer. A copolymer of butyl methacrylate/dimethylaminoethyl methacrylate (80/20) having an average molecular weight of 11,000, and 90% neutralized with acetic acid is used as the acrylic polymer. The recording sheet is printed with an ink jet ink and UV cured as described in Example 6, and would be expected to give similar results.

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What is claimed is:

1. An ink jet recording sheet comprising a support that bears a coating consisting essentially of:

(a) 15 to 80 % by weight of at least one water-soluble vinyl polymer;

(b) 5 to 70 % by weight of at least one acrylic or methacrylic polymer having a number average molecular weight of at least 10,000; and

(c) 5 to 50 % by weight of at least one water-soluble cellulose compound;

wherein said weight % is based on the total weight of said coating composition.

2. The recording sheet of Claim 1 wherein said water-soluble vinyl polymer is selected from the group consisting of polyvinyl pyrrolidone and copolymers thereof, polyvinyl alcohol and copolymers thereof, polyvinylpyridium halide, polyvinylmethylethers, and blends thereof.

3. The recording sheet of Claim 1 wherein said water-soluble vinyl polymer is a substituted hydrophilic polyvinyl alcohol.

4. The recording sheet of Claim 3 wherein the polyvinyl alcohol is selected from the group consisting of N-alkyl styrylpyridinium derivatives of polyvinylalcohol, N-alkyl styrylquinolinium derivatives of polyvinylalcohol, and mixtures thereof.

5. The recording sheet of Claim 1 wherein said acrylic or methacrylic polymer is prepared using at

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least one monomer selected from the group consisting of acrylic acid, methacrylic acid, lower alkyl of 1 to 6 carbon atoms acrylate esters, lower alkyl of 1 to 6 carbon atoms methacrylate esters, styrene, dialkylamino acrylates and dialkylamino methacrylates.

6. The recording sheet of Claim 1 wherein said water-soluble cellulose compound is selected from the group consisting of alkyl cellulose, cyanoalkyl cellulose, carboxymethyl cellulose, carboxyalkyhydroxyalkyl cellulose, hydroxyalkyl cellulose, hydroxyalkylmethyl cellulose wherein the alkyl is 1 to 4 carbon atoms, and partial cellulose esters.

7. The recording sheet of Claim 1 wherein said coating contains a reactive species that improves physical properties of said sheet upon exposure to an external energy source after printing.

8. The recording sheet of Claim 7 wherein said reactive species is present as a substituent group on at least one of component (a), (b), or (c).

9. The recording sheet of Claim 7 wherein said reactive species is present as an additional component in said coating.

10. The recording sheet of Claim 8 wherein the reactive species is selected from the group consisting of acid groups, base groups, epoxy groups, styryl-pyridinium groups, styryl-pyrollium groups, dimethylmaleimide groups, cinnamic groups, unsaturated acrylic groups and bis-azides.

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11. The recording sheet of Claim 10 wherein the reactive species is selected from polyvinyl alcohol derivatives comprising N-alkyl styrylpyridinium or N-alkyl styrylquinolinium groups.

12. The recording sheet of Claim 10 wherein the reactive species is selected from the group consisting of styrylpyridinium acrylates, styrylquinolinium acrylates, styrylpyridinium methacrylates and styrylquinolinium methacrylates.

13. The recording sheet of Claim 10 wherein the reactive species is sodium 4,4'-diazidostilbene-2,2'-disulfonate..

14. The recording sheet of Claim 10 wherein a multivalent metal salt selected from the group consisting of calcium, magnesium, zinc and aluminum is used in combination with the reactive species.

15. The recording sheet of Claim 10 wherein the reactive species is a combination of polyvinyl alcohol acetalized with N-methyl-4-(p-formylstyryl)-pyridinium methosulfate and calcium chloride.