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(54) Title: AQUEOUS INK RECEPTIVE INK JET RECEIVING MEDIUM YIELDING A WATER RESISTANT INK JET PRINT  
 (57) Abstract

An aqueous ink jet receiving medium which yields a water resistant ink jet print and a process for providing a water resistant ink jet print are disclosed. The water resistant ink jet receiving medium comprises an ink receptive layer of a crosslinked vinyl amide acrylic acid or methacrylic acid or ester thereof random copolymer and a cationic resin. The random copolymer employed is preferably a vinyl pyrrolidone/acrylic acid or acrylamide/acrylic acid copolymer.

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**AQUEOUS INK RECEPTIVE INK JET RECEIVING MEDIUM  
YIELDING A WATER RESISTANT INK JET PRINT**

**Field of the Invention**

The present invention relates to an ink jet  
5 receiving medium. In particular, the present invention  
relates to an ink jet receiving medium which yields a  
water resistant ink jet print and a process for  
providing such a water resistant ink jet print.

**Description of Related Art**

10 Printers using sprayable inks, such as ink jet  
printers, have become more popular in recent years due  
to a number of desirable features. Specifically, these  
systems operate quietly at high speed without the need  
for external developing or fixation procedures.  
15 Moreover, through the use of multiple ink jet heads  
various colors may be obtained which are suitable for a  
variety of applications. These printers typically  
employ ink jet heads having small orifices that propel  
ink droplets and are used in various electronic printing  
20 applications. Various methods for ejecting droplets of  
ink have been developed. These methods include the use  
of an electrostatic attraction system, the use of a  
piezoelectric element to impart mechanical vibration or  
displacement to the ink, and pressurizing the ink by  
25 heating. Thus, it is no wonder that such a recording  
method which generates less noise and is capable of  
performing high-speed printing and multi-color printing  
is in great demand.

Ink jet systems are typically comprised of three  
30 components: the printer, the ink and the receptor. The  
printer controls the size, number and placement of the

ink droplets and contains the transport system. The ink provides the colorants which form the image, and the receptor provides the medium which accepts and holds the ink. The quality and stability of the resultant ink jet print is a function of the system as a whole. However, the composition and interaction of the ink and the receptor material most affect the quality and stability of the imaged product.

More specifically, it is desired that the ink be absorbed as rapidly as possible, and that the spread of ink droplets be adequate. The resultant image should be excellent in storability, durability and water resistance.

Ink compositions which are useful in ink jet recording systems are well known and generally contain water, organic solvents and dyes. European Patent 0,294,155 discloses an ink jet composition useful in ink jet recording consisting of a water based vehicle containing about 30-99% wt. water with the balance made up of high boiling solvents such as glycol, glycol ethers, pyrrolidones and amides. The inks contain preferably acid or direct dyes. Optionally, a polyhydric alcohol is added for the prevention of the clogging of nozzles and improvement of ejection stability.

Typically, ink jet systems fall broadly into two categories; those that employ high organic solvent-water based inks, and those that are essentially aqueous. Aqueous inks normally contain up to 10% of a high boiling solvent such as diethylene glycol, whereas high organic solvent inks contain, in addition to water, about 50% of a high boiling organic solvent such as diethylene glycol. The resultant ink jet print using either of these types of ink has poor water resistance (i.e., the dye image leaches out or the image layer

containing the dye dissolves when contacted with water).  
Additionally, the dye image is prone to smudging.

Ink jet film compositions are normally sensitive to water and the print can dissolve and leach out. Also,  
5 under humid conditions, the print can bleed thereby losing definition. This deterioration is accentuated when the inks employ high boiling solvents, such as glycols. Conventional ink jet prints often lack light resistance and good file aging properties as well. A  
10 solution to all the above shortcomings is required to achieve acceptable print stability.

Polymeric films for use as recording media represent a special problem in ink jet recording because their surfaces are hydrophobic or quasi-hydrophobic.  
15 Even when their surfaces are treated with special coatings to accept and absorb the inks, it is difficult to obtain the requisite qualities of image density and resolution without incurring tack, smear, image bleed, water solubilization of the ink receptive matrix, or  
20 other undesirable properties.

The use of water/glycol ink systems presents a special problem. At high humidities, a phenomenon described as image bleed, occurs. The ink jet printer applies small ink droplets in a selective pattern to  
25 form the images. These droplets are absorbed into the coating on the film surface to form dots. After initial absorption, the dye continues to spread laterally. Some post imaging spread is desirable to fill in the white areas between the dots and obtain good image density.  
30 At high humidities, however, this spreading continues and causes the image to spread excessively, that is, to bleed thereby losing image sharpness or resolution. Ink vehicles which do not contain high boiling solvents such as glycol do not exhibit this level of image bleed.

Various attempts have been made to solve these problems in an effort to provide the optimal receptor. Approaches to the problem of hydrophobic surfaces include the use of polymers alone or in admixture as ink receptive coatings; see for example, U.S. Patent Nos. 5 4,503,111; 3,889,270; 4,564,560; 4,555,437 and 4,578,285. Multiple coatings have also been employed in trying to overcome the various problems associated with the hydrophobic nature of recording media; illustrative 10 of these coatings are those described in U.S. Patent No. 4,379,804, Japanese Patent Number 01041589 and Japanese Disclosure Numbers 86-132377; 86-074879 and 86-41549. Additionally, the use of mordants to help fix the dye and minimize bleed has been the subject of a number of 15 patents, including U.S. Patent Nos. 4,554,181; 4,578,285 and 4,547,405.

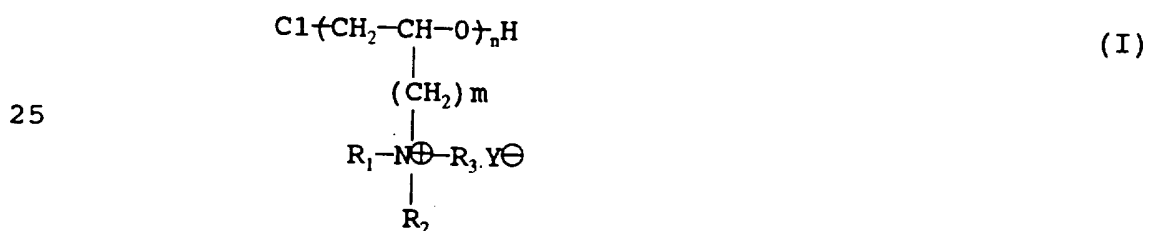
Moreover, there is a strong demand for a recording medium having light transmissivity and a recording medium having gloss on the surface. In these cases it 20 is essential that the surface of the recording medium be non-porous. In this regard, in order to enhance ink affinity and ink receptivity, it has been the practice in the prior art to use a recording medium comprising a non-porous ink-receiving layer formed by use of a water- 25 soluble polymer.

For example, U.S. Patent No. 4,503,111 assigned to Tektronics discloses a recording medium having a non-porous ink-receiving layer formed by using primarily a polyvinylpyrrolidone. However, such a recording medium 30 has various problems. These problems include a recorded image low in light fastness, or that due to the stickiness of the surface of the inked receiving layer, blocking is liable to occur when the printed media are placed upon one another, or when paper is superposed on 35 the recorded surface.

U.S. Patent No. 5,206,071 to Atherton et al. relates to film mediums useful in ink jet printing which films comprise a transparent, translucent or opaque substrate, having on at least one side thereof a water-insoluble, water-absorptive and ink-receptive matrix  
 5 comprised of a hydrogel complex and a polymeric high molecular weight quaternary ammonium salt.

U.S. Patent No. 4,877,680 to Sakaki et al. relates to a recording medium comprising a substrate and a non-porous ink receiving layer. The ink receiving layer  
 10 contains a water-insoluble polymer containing a cationic resin. The recording medium may be employed for recording by attaching droplets of a recording liquid thereon.

U.S. Patent No. 4,576,867 to Miyamoto relates to an ink jet recording paper wherein by attaching a cationic resin having a structure represented by the following general formula (I) to at least the surface of an ink jet recording paper, the water-resistance and the  
 15 20 sunlight fastness of the image formed on the ink jet recording paper can be improved:



wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  represent alkyl group;  $m$  represents  
 30 a number from 1 to 7;  $n$  represents a number from 2 to 20; and  $\text{Y}$  represents an acid residue.

European patent publication 0,500,021 A1 relates to a recording method and recording film comprising a transparent substrate, a porous alumina hydrate layer

formed on the substrate and an opaque porous layer laminated on the alumina hydrate layer.

One of the major drawbacks of an ink jet print has always been the lack of long term durability of the images. Ink jet prints have always been prone to UV light fade, and moisture sensitivity. Since the majority of the ink jet inks currently used in desktop and graphic arts applications are composed mainly of water, the ink jet receiver coatings need to be water receptive. The challenge is to develop a hydrophilic, aqueous ink receptive coating that yields a water resistant ink jet print.

Accordingly, an object of the present invention is to provide a novel recording medium for ink jet recording which is particularly excellent in ink receptivity, sharpness and water resistance.

Another object of the present invention is to provide a recording medium for ink jet recording which is excellent in water resistance, even under highly humid conditions, and also free from migration or leaching of the print ink when water droplets contact the surface of the recorded image, or when left to stand under highly humid conditions.

Still another object of the present invention is to provide a water resistant ink jet print and method thereof.

These and other objects of the present invention will become apparent upon a review of the specification and the claims appended thereto.

30

#### SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a receiving medium comprising a substrate and an ink receiving layer provided thereon,

said ink receiving layer comprising a random copolymer of a vinyl amide and acrylic acid or methacrylic acid or their esters, a cationic resin and a crosslinking agent. Preferably, the random copolymer is a copolymer of  
5 vinylpyrrolidone and acrylic acid or acrylamide and acrylic acid. Upon drying the ink receiving layer subsequent to coating onto the substrate, the random copolymer is preferably crosslinked.

According to another aspect of the present  
10 invention, there is provided a recording medium comprising a substrate and an ink receiving layer provided thereon, said ink receiving layer comprising a 75% vinyl pyrrolidone/ 25% acrylic acid random  
15 copolymer, 10% by weight of a cationic resin and 3 to 4% by weight of a crosslinking agent based on the copolymer. In another aspect, there is provided such a recording medium where the copolymer is an  
acrylamide/acrylic acid random copolymer.

According to a further aspect of the present  
20 invention, there is provided a process for providing a water resistant ink jet print by attaching droplets of a recording liquid on a recording medium, said recording liquid containing a water-soluble dye, water and an  
organic solvent, said recording medium comprising an ink  
25 receiving layer provided on a substrate, with the ink receiving layer comprising a crosslinked vinyl amide acrylic acid or methacrylic acid or ester thereof random copolymer and, a cationic resin.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

30 The present invention relates to an ink jet recording medium. The ink jet recording medium of the present invention comprises a receiving layer which is water resistant and includes a vinyl amide/acrylic acid or methacrylic acid or esters thereof random copolymer,

a cationic resin and a crosslinking agent. The ink receiving layer is generally coated on a suitable substrate and dried to effect crosslinking of the copolymer.

5 Applicants have found experimentally that suitable vinyl amide/acrylic acid or methacrylic acid or esters thereof random copolymers, when properly crosslinked, form the backbone of a water resistant ink jet coating. This coating can be applied to, but is not limited to,  
10 the following substrates: a clear film, a polyethylene clad paper (photobase), adhesive backed vinyl, paper and canvas.

The vinyl amide monomer used in preparing the random copolymer can be derived from either an N-vinyl  
15 amide or a vinyl amide such as acrylamide. The most preferred N-vinyl amide is vinyl pyrrolidone. Acrylamide is another preferred monomer for use in preparing the random copolymer used in the present invention.

20 The monomer copolymerized with the vinyl amide is an acrylic acid or methacrylic acid, or an ester of acrylic acid or methacrylic acid. Among the more preferred acrylates and methacrylates are the methylacrylate, ethylacrylate and methylmethacrylate  
25 esters. It is most preferred, however, that acrylic acid be copolymerized with either vinyl pyrrolidone or acrylamide for purposes of the present invention, as these two copolymers have been found to be most easily available and most useful.

30 International Specialty Products of Wayne, New Jersey manufactures a line of suitable vinyl pyrrolidone/acrylic acid random copolymer products under the trade name Acrylidones. The following table summarizes various characteristics of commercially

available vinyl pyrrolidone/acrylic acid random copolymers.

TABLE 1

	VP/AA RATIO	MOLECULAR WEIGHT	ACID NUMBER
ACP-1001	75:25	250,000	170-210
ACP-1004	50:50	250,000	365-405
ACP-1005	25:75	250,000	560-600
ACP-1033	75:25	80,000	170-210
ACP-1041	50:50	80,000	365-405
ACP-1042	25:75	80,000	560-600

5  
10  
15  
20  
A preferred resin for overall imaging properties contains 75% vinyl pyrrolidone (for example, see ACP-1001 and ACP-1033 above). As the % vinyl pyrrolidone decreases, it has been found that the ink receptivity decreases, generally resulting in poor print quality and long ink dry times. More specifically, it has been found that grades containing 75% vinyl pyrrolidone work the best for print quality and ink dry time, while grades containing 50% vinyl pyrrolidone and 50% acrylic acid are marginal, and grades containing 25% vinyl pyrrolidone and 75% acrylic acid do not receive ink at all.

25  
The preferred acrylamide/acrylic acid copolymers are also commercially available. Suitable copolymers can be obtained, for example, from Cytec Industries Inc. of West Patterson, N.J. under the trademark CYANAMER.

Conventional crosslinking agents are suitable for use in the present invention. However, the aziridine class of polyfunctional crosslinkers is most preferred for the purposes of the present invention. Suitable

aziridine crosslinkers are commercially available, for example, such as crosslinkers CX-100 available from Zeneca Resins of Wilmington, Mass.; XAMA-7 and XAMA-2, both available from Cordova Chemical Co. of North  
5 Muskegeon, Michigan. Such polyfunctional crosslinkers generally have a functionality greater than 2, and more preferably in the range of from 2.5 to 3.5.

In general, the amount of crosslinking agent present is an amount sufficient to crosslink the  
10 copolymer so as to achieve a water resistance that allows the print to be immersed in water while still maintaining the integrity of the coating, and hence the print. It was determined empirically that from about 3 to about 13% of an aziridine crosslinker, based on the  
15 weight of random copolymer, is a preferable amount in terms of print quality and water resistance. More preferably is an amount of from 3 to 5 wt. %, and most preferably from 3 to about 4 wt. %. If too little crosslinker is used, the coatings can be very tacky and  
20 not water resistant at all. If too much crosslinker is used, the coating is generally not very receptive to the aqueous inks, and the resulting prints are poor, with much ink pooling and long ink dry times.

Other conventional crosslinkers such as zirconium  
25 carbonates can also be used with good results.

The crosslinking of the random copolymer is preferably accomplished during the drying step, for purposes of convenience. It may also be accomplished in a separate step, if preferred.

30 Although the crosslinked copolymers work well as a good water resistant backbone for the coating, they are preferably used in combination with a cationic substance. When prints on a coating containing only the crosslinked resin are immersed in water, the coatings  
35 themselves are water resistant, but the ink begins to

bleed and leach out of the coating matrix. Since ink jet dyes typically are anionic in nature, a cationic substance is required to "lock" the dyes in the coating matrix.

5           Conventional cationic resins are suitable for use in the coating of the present invention. Quaternary ammonium compounds are preferable, of these, the higher molecular weight compounds are most preferable and provide the best overall print quality and water  
10 resistance properties. CPS Chemical Company of Old Bridge, New Jersey manufactures several lines of cationic polymers by the trade name of Agefloc, which are suitable for use in the present invention. Of these, a high molecular weight poly (hydroxyalkene  
15 dimethyl ammonium chloride) called Agefloc A-50HV is most preferable with respect to the overall results for print quality and water resistance. Other high molecular weight cationic resins include the Agefloc A-50 and A-40HV.

20           The amount of cationic material used is generally an amount sufficient to preclude bleeding of the ink when the print is immersed in water, i.e., an ink migration precluding amount. It was empirically determined that preferred print quality and water  
25 resistance results are obtained with the use of a formulation containing about 5 to about 10% of the quaternary ammonium resin, as based on the % solids (wt.) of the random copolymer resin. If too little of the quaternary resin is used, the print quality is poor,  
30 and the dye runs when immersed in water. If too much of the quaternary resin is used, the initial print quality is poor, and the coatings are tacky.

          The receiving layer of the present invention can be coated onto a substrate using any conventional coating  
35 process. The coating must generally be dried

sufficiently to assure proper crosslinking. For example, it is generally preferred that the coatings be dried at a minimum of 260°F for about 2 minutes to ensure that the crosslinking cures properly.

5 The present invention also includes a process for providing a water resistant ink jet print. The process includes coating a suitable substrate with a vinyl amide acrylic acid or methacrylic acid or ester thereof random copolymer, a cationic resin and a crosslinking agent;  
 10 curing the coating; and applying droplets of a recording liquid on the coating.

The invention will be illustrated in greater detail by the following specific examples. It is understood that these examples are given by way of illustration and  
 15 are not meant to limit the disclosure or the claims that follow. All percentages in the examples, and elsewhere in the specification, are by weight unless otherwise specified.

**EXAMPLE 1**

20	Syloid 620-----0.06g
	Deionized water-----1.80g
	10% Acrylidone ACP-1001-----87.70g
	28% Ammonium hydroxide-----3.75g
	Xama 7-----0.33g
25	2-Pyrrolidone-----1.09g
	50% Agefloc A-50HV-----1.75g

The above mix was prepared by mixing the Syloid 620 and water on a magnetic stirring plate for 1 minute. The Acrylidone and ammonium hydroxide were added and the  
 30 mixture was stirred on the magnetic stirrer for an additional minute. The final three ingredients (2-pyrrolidone, Agefloc A-50HV, Xama 7) were added, and the mixture was stirred for a final five minutes on a magnetic stirring plate.

The composition was then coated onto 380 gauge Melinex 534 with a gapped number 70 Mayer rod to achieve a coating thickness of about 0.40 mils. The coating was dried in a laboratory Blue M convection oven for 5 minutes at 260° F. This drying step also resulted in the crosslinking of the Acrylidone copolymer.

The sample was then printed on a Canon BJC600 ink jet printer using a full color block test pattern. Visual densities of cyan, magenta, yellow, black, red, green and blue were run using an XRITE 938 color densitometer. The print was allowed to air dry for 1 hour, then it was completely immersed in water for 10 minutes. The visual densities were repeated after the immersion, and calculations were performed to get the % retained density. The results are summarized in Table 2 below.

#### EXAMPLE 2

		Syloid 620-----	0.06g
		Deionized water-----	1.80g
20	10%	Acrylidone ACP-1001-----	78.93g
	28%	Ammonium hydroxide-----	3.75g
		Xama 7-----	0.33g
		2-Pyrrolidone-----	1.09g
	50%	Agefloc A-50HV-----	1.75g
25	10%	Airvol 325-----	8.77g

The above mixture was prepared in the same manner as described in Example 1. The Airvol 325 was added after the Agefloc A-50HV and then the mixture was stirred for the final five minutes. The coating, printing, and water immersion were performed in the same manner as in Example 1. The results are summarized in Table 2 below.

**EXAMPLE 3**

Mix B:

	10%	Gohsenal N-300-----	20.00g
	10%	PVP K90-----	5.00g
5	40%	Zonyl FSJ-----	0.22g
		Water-----	37.00g

Example 3 uses two mixes. The first mix (Mix A) was prepared with the same composition as that in Example 1 and applied to the substrate in the same manner as in Example 1. The second mix (Mix B) was prepared in the following manner:

The Gohsenal N-300 and PVP K90 solutions were blended and mixed for 30 seconds on a magnetic stir plate. The Zonyl FSJ and water were added, and stirred for 5 minutes on a magnetic stir plate.

Mix B was then applied as a topcoat onto the coating of that previously prepared according to Example 1 with a wire wound number 10 Mayer rod. The sample was then dried at 240° F in a Blue M convection oven for 20 minutes.

The sample was then printed, tested, and evaluated in the same manner as in Example 1. The results are summarized in Table 2 below.

**COMPARATIVE EXAMPLE 1**

25		Syloid 620-----	0.06g
		Deionized water-----	1.80g
	10%	Acrylidone ACP-1001-----	87.70g
	28%	Ammonium hydroxide-----	3.75g
		2-Pyrrolidone-----	1.09g
30	50%	Agefloc A-50HV-----	1.75g

The above mixture was prepared in the same manner as described in Example 1. The coating, printing, and water immersion were performed in the same manner as in Example 1. The results are summarized in Table 2 below.

COMPARATIVE EXAMPLE 2

		Syloid 620-----	0.06g
		Deionized water-----	1.80g
5	10%	Acrylidone ACP-1001-----	87.70g
	28%	Ammonium hydroxide-----	3.75g
		Xama 7-----	0.33g
		2-Pyrrolidone-----	1.09g

The above mixture was prepared in the same manner as described in Example 1. The coating, printing, and water immersion were performed in the same manner as in Example 1. The results are summarized in Table 2 below.

Reagents for the above Examples are commercially available according to the following description:

- 1) Amorphous silica is available from W.R. Grace, Baltimore, MD as Syloid 620.
- 2) Vinylpyrrolidone/acrylic acid copolymer is available from International Specialty Polymers of Wayne, NJ as Acrylidone ACP-1001.
- 3) Aziridine crosslinker is available from Cordova Chemical of North Muskegeon, MI as Xama 7.
- 4) Poly (Hydroxyalkene Ammonium Chloride) is available from C.P.S. Chemicals of Old Bridge, NJ as Agefloc A-50HV.
- 5) Fully hydrolyzed polyvinyl alcohol is available from Air Products of Allentown, PA as Airvol 325.
- 6) Prebonded white polyester is available from ICI Films of Hopewell, VA as Melinex 534.
- 7) Fully hydrolyzed polyvinyl alcohol is available from Nippon Gohsei Ltd. of Japan as Gohsenal N-300.

TABLE 2

	PRINT QUALITY	PRINT TACK	AVE. % COLOR DENSITY RETENTION	COMMENTS
EXAMPLE 1	Very Good	Moderate	99.9%	Vibrant colors/Good wet rub resistance
EXAMPLE 2	Very Good	Low	98.8%	Vibrant colors/Good wet rub resistance
EXAMPLE 3	Very Good	Very Low	99.0%	Vibrant Colors/Glossy Finish/Very low print tack
5 COMPARATIVE EXAMPLE 1	Good	Very High	0 %	Coating Washed Off
COMPARATIVE EXAMPLE 2	Poor	Moderate to High	107% High bleed causes increased retention	High color bleed/High Ink coalescence

10 Examples 1 and 2 both had very good print quality and excellent water resistance properties. When a small amount of a fully hydrolyzed polyvinyl alcohol is added, as in Example 2, the print tack is reduced significantly. The print tack can be reduced even further, and the colors can be made very glossy, by
 15 adding a thin PVP/fully hydrolyzed polyvinyl alcohol topcoat as seen in Example 3. In general, the addition or use of small amounts of additional resins, such as polyvinyl alcohol or an acrylic resin, can be employed to improve print quality.

20 When no crosslinker is used, as in Comparative Example 1, the resulting coating is very tacky, and is easily dissolved in water. When the high MW quaternary ammonium resin is eliminated from the mix, as in Comparative Example 2, the print quality is poor

indicating a high amount of bleed and ink pooling. Thus, to achieve an ink jet recording medium which exhibits excellent water resistance and a freedom from migration or leaching, the combination of the random copolymer together with the crosslinker and the cationic resin is important.

EXAMPLE 4

		Syloid 620 -----	0.06g
		Deionized water -----	62.92g
10		Cyanamer P-21 -----	6.99g
	28%	Ammonium hydroxide -----	2.93g
		CX -----	0.29 g
		2-Pyrrolidone -----	0.85g
	50%	Agefloc A-50HV -----	0.75g
15	50%	Fluorad FC-135 -----	0.14g
	20%	Gafquat 755N -----	25.08g

The above mixture was prepared by mixing the Syloid 620 and water on a magnetic stirring plate for 1 minute. The Cyanamer was slowly added, and stirred for 15 minutes. The ammonium hydroxide was added and the mixture was stirred for a final fifteen minutes on a magnetic stirring plate.

The composition was then coated onto 380 gauge Melinex 534 with a gapped number 70 Mayer rod to achieve a coating thickness of about 0.40 mils. The coating was dried in a laboratory Blue M convection oven for 5 minutes at 260 F.

The samples were then printed on a Canon BJC600e ink jet printer, and an Encad NovaJet ink jet printer using a full color block test pattern. The print was allowed to air dry for 1 hour, then it was completely immersed in water for 10 minutes. The print quality, evaluated as in Example 1, water immersion and wet rub resistance were all very good.

The reagents used in the foregoing Example are commercially available and may be generally described as follows:

5           Syloid 620 -- amorphous silica from W.R. Grace,  
            Baltimore, Md.

            Cyanamer P-21 -- acrylamide/acrylic acid copolymer  
            from Cytec Industries Inc. of West Patterson, N.J.

            CX-100 -- aziridine cross linker from Zeneca Resins  
            of Wilmington, Ma.

10           Agefloc A-50HV -- poly(Hydroxyalkene ammonium  
            chloride) from C.P.S. Chemicals of Old Bridge, N.J.

            Fluorad FC-135 -- cationic fluorosurfactant from 3M  
            of St. Paul, Minnesota

15           Gafquat 755N -- quaternized copolymer of  
            vinylpyrrolidone and dimethylaminoethyl  
            methacrylate from International Specialty Products  
            of Wayne, N.J.

            Melinex 534 -- prebonded white polyester from ICI  
            Films of Hopewell, Va.

20           While the invention has been described with  
            preferred embodiments, it is to be understood that  
            variations and modifications may be resorted to as will  
            be apparent to those skilled in the art. Such  
            variations and modifications are to be considered within  
25           the purview and the scope of the claims appended  
            thereto.

**WHAT IS CLAIMED IS:**

1. An ink jet receiving medium having an ink receptive coating comprised of a random copolymer of a vinyl amide and an acrylic or methacrylic acid or an ester thereof, a cationic resin and a crosslinking agent.
2. The ink jet receiving medium of Claim 1, wherein the random copolymer is a copolymer comprised of vinyl pyrrolidone.
3. The ink jet receiving medium of Claim 2, wherein the random copolymer is a copolymer comprised of acrylic acid.
4. The ink jet receiving medium of Claim 1, wherein the random copolymer is a copolymer comprised of acrylamide.
5. The ink jet receiving medium of Claim 4, wherein the random copolymer is a copolymer comprised of acrylic acid.
6. The ink jet receiving medium of Claim 1, wherein said vinyl pyrrolidone/acrylic acid random copolymer is comprised of 75% vinyl pyrrolidone and 25% acrylic acid.
7. The ink jet receiving medium of Claim 1, wherein said crosslinking agent is present in an amount of from 3 to 4% by weight, as based on the random copolymer.
8. The ink jet receiving medium of Claim 1, further comprising a substrate which is a clear film, a

polyethylene clad paper, adhesive backed vinyl, paper or canvas.

9. The ink jet receiving medium of Claim 1, which is obtained upon crosslinking the random copolymer.

10. An ink jet receiving medium comprising a substrate, an ink jet ink receptive coating on said substance comprised of a crosslinked vinyl acrylic acid or methacrylic acid or ester thereof random copolymer and a cationic resin.

11. The ink jet receiving medium of Claim 10, wherein the random copolymer is a copolymer comprised of vinyl pyrrolidone.

12. The ink jet receiving medium of Claim 11, wherein the random copolymer is a copolymer comprised of acrylic acid.

13. The ink jet receiving medium of Claim 10, wherein the random copolymer is a copolymer comprised of acrylamide.

14. The ink jet receiving medium of Claim 13, wherein the random copolymer is a copolymer comprised of acrylic acid.

15. A water resistant ink jet print comprising a substrate, an ink receptive coating on said substrate with said coating comprising a crosslinked vinyl amide acrylic acid or methacrylic acid or ester thereof random copolymer and a cationic resin; and, an image on said ink receptive coating.

16. The ink jet receiving medium of Claim 15, wherein the random copolymer is a copolymer comprised of vinyl pyrrolidone.

17. The ink jet receiving medium of Claim 16, wherein the random copolymer is a copolymer comprised of acrylic acid.

18. The ink jet receiving medium of Claim 15, wherein the random copolymer is a copolymer comprised of acrylamide.

19. The ink jet receiving medium of Claim 18, wherein the random copolymer is a copolymer comprised of acrylic acid.

20. A process for providing a water resistant ink jet print comprising  
attaching droplets of an aqueous recording ink containing a water-soluble dye to a receiving medium comprising an ink receiving layer provided on a substrate, the ink receiving layer comprising a crosslinked vinyl acrylic acid or methacrylic acid or ester thereof random copolymer and a cationic resin.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/16371

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 3/00  
US CL : 428/195

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/195, 211, 409, 500, 537.5

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,101,218 (SAKAKI ET AL.) 31 March 1992, see entire document.	1-20

Further documents are listed in the continuation of Box C.       See patent family annex.

<p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>*&amp;* document member of the same patent family</p>
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**28 MARCH 1996**

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