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(54) **INKJET RECEPTOR MEDIUM HAVING INK MIGRATION INHIBITOR AND METHOD OF MAKING AND USING SAME**

TINTENSTRAHLEMPFANGSMEDIUM MIT EINEM TINTENMIGRATIONSINHIBITOR, UND VERFAHREN ZU DESSEN HERSTELLUNG

SUPPORT RECEPTEUR DE JET D'ENCRE COMPORTANT UN INHIBITEUR DE FLUX D'ENCRE ET PROCEDES DE FABRICATION ET D'UTILISATION CORRESPONDANTS

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Description

[0001] The file of this patent contains at least one drawing executed in color. Copies of this patent with color drawings will be provided by the Patent and Trademark Office upon request and payment of the necessary fee.

[0002] This invention relates to a microporous inkjet receptor that provides excellent images with pigmented inks deposited thereon in a manner that impedes migration of the pigmented inks when in contact with water. Furthermore, the present invention relates to a method of using a pigmented ink migration inhibitor

[0003] Inkjet imaging techniques have become vastly popular in commercial and consumer applications. The ability to use a personal computer and desktop printer to print a color image on paper or other receptor media has extended from dye-based inks to pigment-based inks. The latter provide brilliant colors and more durable images because pigment particles are contained in a dispersion before being dispensed using a thermal inkjet print head, such as those commercially available from Hewlett Packard Corporation or LexMark Corporation in inkjet printers commercially available from Hewlett Packard Corporation, Encad Inc., Mimaki Corporation, and others.

[0004] Ink jet printers have been in general use for wide-format electronic printing for applications such as, engineering and architectural drawings. Because of the simplicity of operation, economy of ink jet printers, and improvements in ink technology the inkjet imaging process holds a superior growth potential promise for the printing industry to produce wide format, image on demand, presentation quality durable graphics.

[0005] The components of an ink jet system used for making graphics can be grouped into three major categories:

1 Computer, software, printer.
2 Ink.
3 Receptor sheet.

[0006] The computer, software, and printer will control the size, number and placement of the ink droplets and will transport the receptor film. The ink will contain the colorant or pigments which form the image and the receptor film provides the medium which accepts and holds the ink. The quality of the ink jet image is a function of the total system. However, the composition and interaction between the ink and receptor film is most important in an ink jet system.

[0007] Image quality is what the viewing public and paying customers will want and demand to see. Many other demands are also placed on the ink jet media/ink system from the print shop, such as rapid drying, humidity insensitivity, extended shelf life, waterfastness and overall handleability. Also, exposure to the environment can place additional demands on the media and ink (depending on the application of the graphic).

[0008] Porous membrane is a natural choice to use as an ink jet receptive media because the capillary action of the porous membrane can wick the ink into the pores much faster than the absorption mechanism of film forming water soluble coatings. However, in the past, when a porous coating or film has been employed to achieve desired quick dry, optical density has suffered greatly because the colorant penetrates too deep into the porous network. This type of problem is magnified by printers that dispense high volumes of ink per drop because extra film thickness may be required to hold all the ink. When the pore size and pore volume of the membrane are opened to allow the pigments to penetrate, the pigments can be stratified in the membrane. Meaning, the black, cyan, magenta, and yellow will be predominately found at different depths depending on the order of application. Hence, some of the first color(s) applied is /are optically trapped in the image by subsequent application of other pigmented ink. Furthermore, lateral diffusion of the ink can also be a problem inherent in porous membranes used as receptive media. When pigmented inks are jetted onto a porous film that has a pore size that is too small, color pigments will be filtered on the top of the membrane rendering high image density, but the pigments could easily smear and have the effect of never drying. Also, excess fluid from the ink can coalesce, or even worse, pool and run on the image before the water/glycol carrier is wicked away.

[0009] The chemical formulation of the pigmented inkjet ink has considerable complexity due to the requirement of continued dispersion of the pigment particles in the remainder of the ink and during jetting of the ink.

[0010] The typical consumer medium for receiving dye-based inkjet inks has been paper or specially coated papers. However, with too much inkjet ink in a given area of the paper, one can see the over-saturation of the paper with the aqueous ink in which dye was dissolved.

[0011] As inkjet inks have become more commercially oriented and pigmented-based inks have become more prevalent, different media have been tried in an attempt to control the management of fluids in the ink.

[0012] Japanese Patent JP 61-041585 discloses a method for producing printing material using a ratio of PVA/PVP. The disadvantage is inadequate waterfastness and wet rub off properties.

[0013] Japanese Patent JP61-261089 discloses a transparent material with cationic conductive resin in addition to a mixture of PVA/PVP. The material is water fast and smudge proof but the wet rub off properties are poor.

[0014] European Patent Publication EP 0 716 931 A1 discloses a system using a dye capable of co-ordinate bonding with a metal ion in two or more positions. Again binder resins are used with inorganic pigments in the paper or film. The metal ion was preferred to be jetted on before imaging and additional heating is necessary to complete the reaction.

This system was not claiming to be water fast; the focus was long term storage without fading from heat or light.

[0015] U.S. Pat. No. 5,537,137 discloses a system to achieve waterfastness by curing with heat or UV light In the body of the patent, examples of their coatings contained Ca++ from $CaCl_2$. This was added to provide reactive species for the acid groups on the dispersed polymer. The coating remains water soluble until UV or heat curing after imaging.

[0016] Hence, the current special ink jet media employ vehicle absorptive components, and sometimes optional additives to bind the inks to the media. As a consequence current media are inherently moisture sensitive and can be fragile to handling and subject to finger smearing. Moreover, the vehicle absorptive components usually consist of water soluble (or swelling) polymers which result in slower printing speeds and dry times.

[0017] Pigmented ink delivery systems have also dealt with pigment management systems, wherein the resting location of the pigment particles are managed to provide the best possible image graphic. For example, U.S. Pat. 5,747,148 (Wamer et al.), discloses a pigment management system in which a suitable supporting layer (including in a listing a microporous layer) has a two layer fluid management system: a protective penetrant layer and a receptor layer, both layers containing filler particles to provide two different types of protrusions from the uppermost protective penetrant layer. Electron microphotographs in that application show how the pigment particles of the ink encounter smooth protrusions that provide a suitable topography for pigment particle "nesting" and rocky protrusions that assist in media handling and the like.

[0018] Other ink receptors have been disclosed, including U.S. Pat. Nos. 5,342,688 (Kitchin): 5,389,723 and 4,935,307 (both Iqbal et al.); 5,208,092 (Iqbal) 5,302,437 (Idei et al); U.S. Pat. No. 5,206,071 (Atherton et al.); and EPO Patent Publication 0 484 016 A1.

[0019] WO-A-96/18496 describes 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. 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.

[0020] It has been found that inkjet receptor media requires durability for exposure to water in the form of humidity, rain, dew, snow, and the like.

[0021] It has also been found that pigment particles in aqueous inkjet ink formulations require time to establish a stable relationship with the medium upon which they have been deposited during inkjet printing.

[0022] It has been found that pigment particles are capable of migration within pores of a porous inkjet receptor medium, even if such receptor medium has both a fluid management system and a pigment management system.

[0023] What the art needs is an inkjet receptor medium that assures rapid establishment of a stable relationship between pigment particles (and their dispersants) and the inkjet receptor medium, particularly when the printed medium is likely to be exposed to water or other solvents shortly after printing.

[0024] The present invention describes a migration inhibitor for pigmented inks comprising a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water.

[0025] For purposes of this application, "soluble in water" means dissolution of the monomer in deionized water at room temperature (about 15-18°C) at a rate of 50-90 grams/100g of water. By contrast, "sparingly soluble in water" means the monomer is capable of being dispersed in deionized water at room temperature (about 15-18°C) without becoming substantially dissolved (no more than about 1 gram/100 grams of water) in that deionized water, notwithstanding possible solubility in blends of water and other hydrophilic solvents.

[0026] The present invention describes a homopolymer or copolymer that has hydrophilic interaction sites for both pigmented particles and their associated dispersants and hydrophilic interaction sites for multivalent metal ion coordination. "Hydrophilic interaction" in the present context means a physicochemical phenomenon whereby the functional group(s) in the homopolymer or copolymer undergoes interactions with the dispersants and the metal ions in hydrophilic medium.

[0027] One advantage of the present invention is that a dispersible-co-soluble hydrophilic homopolymer or copolymer described in the present invention can substantially immobilize pigment particles and their associated dispersants from migration when the printed inkjet receptor medium comes in contact with water.

[0028] The present invention provides an inkjet receptor medium, comprising (a) a porous membrane or porous film suitable to be ink jet printed with pigmented ink, and (b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water; wherein the number average molecular weight of the copolymer ranges from 20,000 to 200,000.

[0029] Furthermore, the present invention provides an inkjet receptor medium, comprising (a) a porous membrane or porous film suitable to be ink jet printed with pigmented ink, and (b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water; wherein the porous membrane or porous film is selected from a microporous membrane impregnated with a microporous fluorinated silica agglomerate together with a binder and a surfactant or a combination of surfactants; and a microporous membrane impregnated with inorganic multivalent metal salt together with a surfactant or combination of surfactants.

[0030] Moreover, the present invention provides an inkjet receptor medium, comprising (a) a porous membrane or porous film suitable to be ink jet printed with pigmented ink, and (b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water; wherein the porous membrane or porous film is a Thermally Induced Phase Separated microporous membrane.

[0031] In addition, the present invention provides a method of using a pigmented ink migration inhibitor, comprising the step of coating as a solution a copolymer as defined above on and into a surface of a porous membrane or film.

[0032] Other features and advantages of the invention will be disclosed in relation to the embodiments of the invention, using the following drawings.

Fig. 1 is a comparison color photograph showing pigment migration when inkjet receptor medium has not employed the pigment migration inhibitor of the present invention.

Fig. 2 is a color photograph showing substantially no pigment migration under the same conditions as seen in Fig. 1, except that the inkjet receptor medium has employed the pigment migration inhibitor of the present invention.

Inkjet Receptor Medium

[0033] The inkjet receptor medium can be any porous membrane or film known to those skilled in the art wherein it is desired to print inkjet inks on at least one major surface thereon. Preferably, the medium comprises an inkjet receptor medium, comprising a porous substrate having a fluid management system and having a pigment management system in contact with surfaces of pores of the substrate therein. One embodiment of that medium is an inkjet receptor comprising a microporous membrane impregnated with an inorganic multivalent metal salt together with a surfactant or combination of surfactants chosen for the ink and membrane being employed.

[0034] Another embodiment is an inkjet receptor comprising a microporous membrane impregnated with a microporous fluorinated silica agglomerate together with a binder and a surfactant or a combination of surfactants for the ink and membrane being employed.

[0035] Another embodiment is an inkjet receptor comprising a microporous membrane impregnated with a microporous fluorinated silica agglomerate together with a binder and a surfactant or combination of surfactants wherein the surfactants are selected from the group of hydrocarbon-based anionic surfactants, silicon-based non-ionic surfactants or fluorocarbon-based non-ionic based surfactants or a combination thereof.

[0036] These receptors, when imaged in an inkjet printer, provide very high density and very high quality images which are tack-free and instantaneously dry to touch.

[0037] The ink colorant is typically a pigment dispersion having a dispersant that binds to the pigment and that will destabilize, flocculate, agglomerate, or coagulate the pigments on contact with the media component Depositing each of the colors at or just below the surface of the membrane allowing the carrier fluid to wick into the membrane where the fluid management system can take over while providing a sheltered location for the pigments as managed by the pigment management system.

[0038] More preferably, the inkjet receptor medium uses a Thermally Induced Phase Separated (T.I.P.S.) microporous membrane disclosed in U.S. Pat. No. 4,539,256 (Shipman) and available from 3M. For optimization, the pore size and pore volume of the porous film can be adjusted for the model or make of the ink jet printer to correctly hold the volume of ink dispensed by the printer ensuring the highest possible image quality. The coating on the preferred media/ink set has special utility in the demanding ink jet printing applications found in commercial printing. Thus, one can "fine tune" the properties of these receptors to deal with the variables of inkjet ink delivery, including without limitation: porosity of media, pore size, surface wetting energy, and other capacity issues for media to receive ink of various formulations and drop volumes. Moreover, these media exhibit a complex porosity in its porous material that provides both a tortuous path for fluid management and a tortuous path that ensnares the pigment initially and continually, during ink delivery.

Pigment Migration Inhibitor

[0039] Pigment migration inhibitors useful in the present invention can be homopolymers or copolymers having any number of hydrophilic monomers, each of whose homopolymers are hydrophilic, so long as the resulting copolymer is sparingly soluble in water, as defined above.

[0040] Nonlimiting examples of hydrophilic monomers are methacrylic, ethacrylic acids, acrylic acid N-vinylphthalimide, vinylimidazole, vinylpyridine and N-vinyl-2-pyrrolidnone, with the last and acrylic acid being presently preferred.

The homopolymer used in the present invention is a polyvinylpyrrolidinone (PVP) of relatively high molecular weight available from commercial sources.

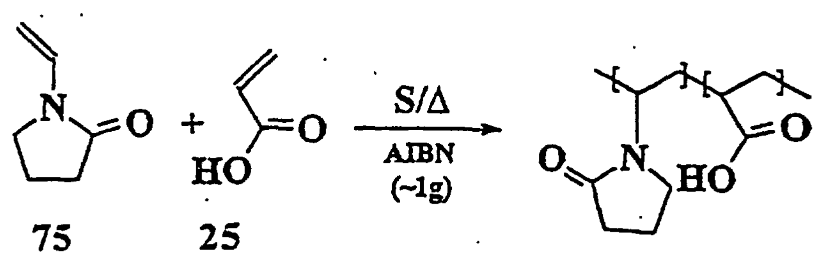
[0041] Molecular weight (Number Average) has been been found to be significant for performance of the inhibitor homopolymer or copolymers of the present invention. The molecular weight of the homopolymer can range from about 10,000 to about 2,000,000 and preferably from about 500,000 to about 1,500,000. The molecular weight of the copolymer can range from about 10,000 to about 300,000 and preferably from about 20,000 to about 200,000 and more preferably from about 30,000 to about 100,000 (greater than about 35,000.). Very high molecular weight copolymer tends not to be soluble in the coating composition. The intermediate molecular weight copolymer e.g., from 30,000-100,000 as used in the present invention is fairly soluble under hot-water treatment and is therefore, workable.

[0042] Once monomers are selected, the polymerization is rather less complicated. Mixing the monomers in appropriate solvent with the right amount of initiator and subjecting the mixture to mild heating allows polymerization reaction to take place in reasonable time frame. The initiator concentration has to be adjusted in such a way so that in a given set of monomer concentrations, the copolymer with the desired molecular weight is obtained with 95-99% conversion.

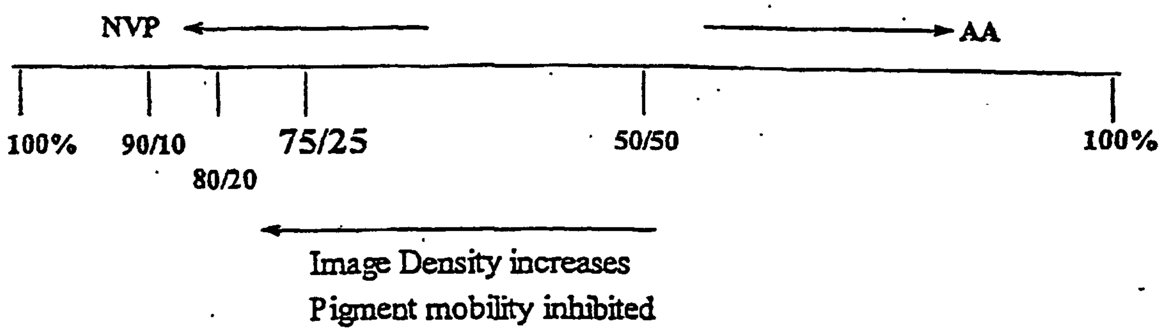
[0043] Use of appropriate solvent for the copolymerization is another important aspect in the preparation of the copolymer. In such etheral solvent as THF, the reaction is very exothermic as it is in related hydrocarbon solvents. In such solvents, the polymer is formed as precipitates which is subsequently obtained by filtration via a preferable treatment in a non-solvent. Due to high exothermicity, use of such solvent is less desirable.

[0044] It is, however, more desirable to make use of such a solvent as an alcohol e.g., an ethanol which is an integral part of the coating composition. The copolymer has been prepared in methanol, ethanol and isopropanol. In methanol, the resulting copolymer is relatively more soluble and in isopropyl alcohol, it is less soluble. In ethanol, the copolymer was obtained as partly soluble and partly insoluble material; at the end of reaction the material was dissolved by adding the required amount of water to obtain a clear solution. The amount of water added is such that a definite workable concentration of the copolymer can be obtained in the mixed solvent.

[0045] The comonomer ratios determining composition of the copolymer is important. These ratios reflect not only the solubility of the copolymer in water-based composition but also determines the copolymers' inhibitor properties towards the pigment mobility. A copolymer of acrylic acid and (N-vinyl-2-pyrrolidinone) provides a balance of properties for both high density and low pigment mobility and does not adversely interfere with other properties such as fluid management and other pigment management such as flocculation/agglomeration of the pigment particles. The copolymer consisting of N-vinyl-2-pyrrolidinone ["NVP"] and acrylic acid ["AA") in the ratio from 70-80% to about 30-20% is preferable and from 75-90% to about 25-10% is more preferable for the present invention. The inhibition vs. image density as part of the copolymer properties is shown in the following profile:



S = THF, Ethanol, Methanol, isopropyl alcohol



M_w = ~44,000, M_n = ~27,000, Pd = 1.63
~95% conversion/ 4-6 hr reaction

[0046] Copolymerization can be performed according to an anionic polymerization procedure as disclosed in Hornby et al., Soap/Cosmetics/Chemical Specialties, June 1993.

[0047] Once monomers are selected, the polymerization of them has been found to be significant for performance of the inhibitors of the present invention. The weight percent ratio of (monomer dispersible in water such as NVP): (monomer soluble in water such as AA) can range from about 65:35 to about 90:10, and preferably about 75:25.

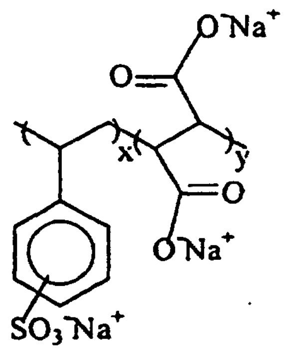
[0048] Polymerization of hydrophilic monomers to form a copolymer can employ any conventional polymerization technique, among included, bulk polymerization, emulsion polymerization, solution polymerization, with the last being presently preferred. Such polymerization processes can be effected by conventional procedures, among included, anionic, free-radical polymerizations, with the last being presently preferred.

[0049] After polymerization of the inhibitor copolymer, the inhibitor copolymer is added to a coating solution. The weight percent of the inhibitor homopolymer or copolymer in the coating solution can range from about 0.1 to about 5% in order to minimize deleterious effects on other printing properties, and preferably from about 0.3 to about 3 weight percent, and more preferably from about 0.5 to about 2% weight percent.

[0050] Use of some hydrophilic copolymers consisting of monomers being more hydrophilic and water soluble, provides enhanced image density but does not allow significant pigment inhibition in the present composition or they may interefere with other fluid management and pigment management properties such as dry time, smudge resistance, and the like. Some of such hydrophilic copolymers are shown below:

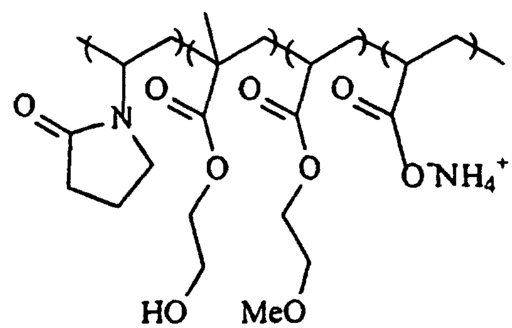
Sulfonated Styrene-Co-Maleic Anhydride ("SSMA"):

[0051] This copolymer was prepared from styrene/maleic anhydride (3:1) and then the aromatic was sulfonated. Alkaline hydrolysis of the material gave hydrophilic sulfonated styrene-maleic acid copolymer in sodium-salt form



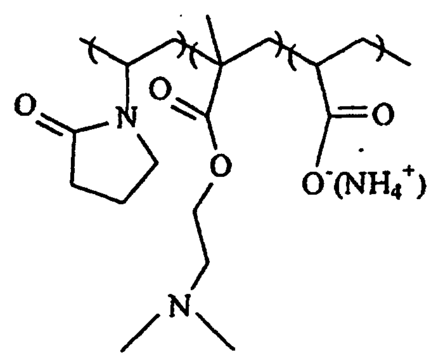
4-Component Copolymer:

[0052] This copolymer consisting of NVP/HEMA/MEA/AA(NH,) in the ratio 60:20: 10: 1 Oenhanced the ink densities but does not significantly inhibit pigment migration



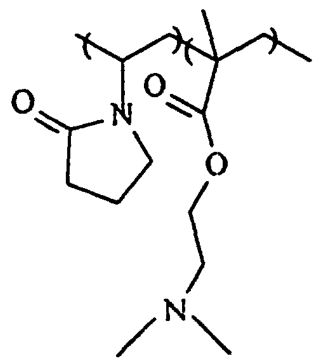
3-Component Copolymer:

[0053] This copolymer consisting of NVP/DMAEMA/AA(NH_4^+) in the ratio 70:20: 10 enhances the ink densities but does not significantly inhibit pigment migration.



Copolymer 958:

[0054] This material consisting ofNVP/DMAEMA in the ratio 20:80 enhances the ink density but does not significantly inhibit pigment migration.



Copolymer 845:

[0055] This material consisting of NVP/DMAEMA in the ratio 80:20 significantly enhances the ink density.

[0056] Yet some copolymers with both hydrophilic and hydrophobic monomers renders inhibition to the pigment mobility to a lesser extent compared to the homopolymer or the copolymer used in the present invention. Some of these copolymers are shown below:

Acrylic Resin:

[0057] This material, a Carboset brand acrylic polymer containing styrene units (from B.F.Goodrich) helped reduce the black pigment mobility onto the substrate to a significant extent.

Vancryl-454:

[0058] This is an ethylacrylate, methylacrylate and methacrylic acid copolymer (from Air Products) helped reduce the black pigment migration onto the substrate to a significant extent.

Latex:

[0059] Some of the latices consisting of both hydrophilic and hydrophobic monomers were also used to inhibit pigment mobility. Examples of such latices are copolymer of ethylene and vinylacetate, (Airflex) from Air products, copolymers of styrene and NVP from ISP. These copolymers did not effect pigment inhibition owing to their latex characetistics-they tend to plug the pores in the porous film.

Cross-linkers:

[0060] Effecting pigment inhibition on the porous film was attempted by making use of certain cross-tinkers e.g., aziridine couplers in the coating composition. CX-100 (from Zeneca) a liquid water-soluble cross-linker and XAMA-7 (from Ciba-Geigy) a semi-liquid wafer-ethanol soluble cross-linker were used in 0.5-1 % range in the coating composition. Use of these cross-linkers moderately improved the black pigment fixation on the receptor on water-challenge.

[0061] Other ink receptive copolymers that are sparingly soluble in water include a copolymer of N-vinylpyrrolidone, acrylic acid, and trimethoxysilylethylmethacrylate (80/10/10); a copolymer of N-vinylpyrrolidone, acrylic acid, trimethoxysilylethylmethacrylate, and ethyleneoxide acrylate (75/10/5/10); a copolymer of N-vinylpyrrolidone, acrylic acid, and N, N, N-methyloctylheptadecafluorosulfonylethylacrylate (MeFOSEA) (80/10/10); a copolymer of N-vinylpyrrolidone, acrylic acid, trimethoxysilylethylmethacrylate and N, N, N-ethyloctylheptadecafluorosulfonylethylacrylate (EtFOSEA) (83/10/2/5); and); a copolymer of N-vinylpyrrolidone, acrylic acid, and Sulfonated Styrene--Sodium Salt (60/10/30).

<u>Optional Additives</u>

[0062] In addition to the migration inhibitor described in the present invention, one can add other compounds to improve image quality and stability. For example, to overcome the presence of any residue residing on the exposed surface of a porous inkjet medium, where the pigment particles are supposed to be nested within the porous surfaces of the medium, one can add a drying agent to the coating solution used to load a fluid management system and/or a pigment management system to a porous medium. Pigment drying agents useful in the present invention can be an aromatic or aliphatic acids having sulfonic, carboxylic, phenolic or mixed functionalities thereof.

Usefulness of the Invention and Examples

[0063] It has been found that ink migration of the pigment particles can occur when a portion of a printed inkjet medium protected by an overlaminate is partially submerged in water and capillary forces cause *continuous* water flow within the overlaminated printed medium within the submerged portion to other locations within the submerged portion and sometimes to the unsubmerged portion. This continuous water flow in true capillary action transports pigment particles within various locations in the submerged portion and sometimes to the unsubmerged portion, leaving transported pigment particles in unintended locations which distorts the intended image. This phenomenon can be noticeable within minutes or can occur only after several hours of submersion of a portion of the printed ink. This noticeable ink migration is in a manner like thin layer chromatography. The compositions described in the present invention inhibit this ink migration, delaying the phenomenon from minutes to weeks or more. Any edge of a laminated printed inkjet image or a disruption in the overlaminate can be a source for water flow or capillary action. Pigment migration could occur unless the compositions of the present invention are employed to inhibit pigment migration. The amount of water flow via capillary action can also determine the amount of migration, but printed inkjet images should be designed for possible severe conditions than to risk loss of image quality or image assurance.

[0064] Fig. 1 shows a color photograph of several colors of HP2500 Series brand pigmented inkjet inks (commercially available from Hewlett Packard Corporation of Palo Alto, CA, USA) printed in an image of a test pattern on an inkjet receptor medium, namely, an oil-in microporous polypropylene membrane prepared according the disclosures of U.S. Pat. Nos. 4,539,256 (Shipman et al.), 4,726.989 (Mrozinski), and more particularly 5,120,594 (Mrozinski), treated with

Aluminum sulfate, tetradecahydrate	4.1%
Dioctylsulfosuccinate (Dos^3)	7.0%
5-Sulfoisophthalic Acid-Na(mono) salt	13.8%
Ethanol/IPA	25%
De-ionized water	50.1%

This membrane had the following properties:

Bubble point	0.9 µm
Gurley 50cm^3	15 sec
Porosity % void	38 %
Surface wetting Energy (before treatment)	30 dynes/cm2
Caliper	0.178 mm (7 mil)

The composition was coated onto the microporous inkjet receptor medium with a No. 4 Meyer bar. The printed medium was laminated with 3M Scotch No. 845 Book Tape and the laminated medium was adhered to a piece of anodized aluminum and approximately 75% percent was submerged in water for a period of about 4 hours. During this time of submersion, the image deteriorated due to pigment migration. Moreover, via capillary action, the pigment also wicked above the water line as seen in Fig. 1.

[0065] Fig. 2 shows a repeat of the same experiment as seen in Fig. 1, except that the formula was modified to add to coating solution 2 weight percent of N-vinyl-2-pyrrolidone-co-acrylic acid copolymer in a weight ratio of 75:25 and having a molecular weight (MWn) of about 96,000. The submersion resulted in substantially no underwater pigment migration nor wicking of any color to the waterline or above the waterline for 4 days under eye examination. Similar experiments have been run for as long as 10 days also demonstrate the properties of this invention, although failure of the test for migration will be seen usually within the first 2 days. It is presently believed that the inhibition of this invention continues indefinitely and longer than any anticipated length of image display in water-containing environments.

[0066] Work was also done replacing NVP/AA copolymer coating used in the example seen in Fig. 2 with 1,300,000 M.W. (Number Average) polyvinyl pyrrolidinone [PVP] in 0.6 wt% to obtain the similar excellent results.

[0067] Appropriate drying/heating the coated receptor prior to imaging is another important parameter in the design and development of the present high ink-volume microporous inkjet receptor. It was found that lack of appropriate drying can cause the ink (pigment) to migrate in the under-water test even though all other conditions are satisfied. It was, further, found that hand-held heat guns could cause insufficient or uneven drying of the receptor. A uniform ovendrying the receptor after coating from 90°C to about 120°C for about 1-3 mins and more preferably for about 1-1.5 mins provides sufficient drying to induce chemical-fixation of the ingredients, components or compounds of the composition into the porous film. Then the coated, dried membrane can be stored for a considerable period of time (at least one year) before printing. The procedure allows no pigment migration in any of the water tests described for an indefinite period of time.

[0068] Another test for pigment movement or migration from water is the following water spray test:

Water Spray Test

Tempered water from a standard 1.90 cm (¾ inch) aerated faucet was allowed to drop 0.61 meters (2 feet) at a rate of 6 liters per minute for 5 minutes onto the coated film sample which was imaged with a test pattern (the same pattern as seen in figures 1 and 2). The sample was moved about so each color area could receive the water stream directly. The sample was removed from the water stream, allowed to dry and observed for ink movement. For ease and documentation of this test, each sample was adhered to an aluminum plate and the test was performed about 10 minutes after printing.

[0069] Imaged membranes benefitting from the present invention pass this Water Spray Test.

[0070] While not being limited to a particular theory, it is believed that the dispersants, surrounding a pigment particle that have not yet become agglomerated have nonetheless become associated with the migration inhibitor copolymer through hydrophilic interaction. Moreover, the molecular weight of the migration inhibitor copolymer results in establishment of pigment stability in the medium because of the tortuous path within the porous medium is far less likely to permit capillary action for a pigment particle associated with a homopolymer or copolymer having such molecular weight or the copolymer having reduced hydrophilicity.

[0071] The work seen in Figs. 1 and 2 was repeated successfully using a microporous membrane prepared using thermally induced phase separation techniques according the disclosures of U.S. Pat. Nos. 4,539.256 (Shipman et al.), 4,726,989 (Mrozinski), and more particularly 5,120,594 (Mrozinski). This membrane had the following properties:

Bubble point	0.75 μm
Gurley $50cm^3$	20 sec
Porosity % void	41%
Surface wetting Energy (before treatment)	30 $dynes/cm^2$
Caliper	0.178 mm (7 mil)

[0072] The membrane was treated with a coating of

Aluminum sulfate, tetradecahydrate	3.3%
Dihexylsulfosuccinate	6.0%
5-Sulfoisophthalic Acid-Na(mono) salt	7.0%
Phthalic acid	4.0%
Ethanol/IPA	26%
De-ionized water	53.7%.

[0073] The example was repeated with another piece of the same membrane, which was also impregnated with another coating solution consisting of:

Aluminum sulfate, tetradecahydrate	5.0%
Dicyclohexylsulfosuccinate	6.0%
D,L-2-Pyrrolidone 5-carboxylic acid	5.0%
5-Hydroxyisophthalic acid	4.0%
Polyvinylpyrrolidone-co-acrylic acid	2.0%,
Isopropyl alcohol	30%
Deionized water	48%

[0074] The dry membrane was imaged with an HP 2500 Series Printer to obtain a very high density, dry, and smudge-free image which was resistant to wet-rub and water migration immediately after printing.

[0075] The experiment was repeated, without migration inhibitor, using a different coating solution of

Aluminum sulfate, tetradecahydrate	5.75 %
Dioctylsodiumsulfosuccinate	9.0%
Silwet L 7607	0.75%
Surfynol 104PA	2.25%
Isopropyl Alcohol	25.0%
Deionized Water	57.25%

[0076] After coating and drying, the membrane was imaged with an Encad printer fitted with 3M inks. The image was overlaminated with a 3M product called #8519 from the Commercial Graphics Division, and partially submerged in water. The black and cyan pigments began to move in less than 20 minutes as the water traveled through the membrane.

[0077] The experiment was repeated with the same coating solution except that 2.0% polyvinylpyrrolidone-co-acrylic acid (75/25) was added to the receptor solution, reducing the water accordingly. After imaging and overlaminating with #8519. the image was partially submerged in water for 24 hours where it was observed that no ink had migrated from its original location.

[0078] It has been observed that not only does the migration inhibitor of the present invention minimize pigment migration as water enters into the imaged membrane, but also the pigment migration is minimized as water recedes. Thus, the image is preserved as much as possible regardless of the location of water about the membrane and which way the water is moving.

[0079] The invention is not limited to the above embodiments. The claims follows.

Claims

1. An inkjet receptor medium, comprising

    (a) a porous membrane or porous film suitable for being ink jet printed with pigmented ink, and

    (b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising
    a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water;

    wherein the number average molecular weight of the copolymer ranges from 20,000 to 200,000.

2. The medium of Claim 1, wherein the copolymer has a number average molecular weight ranging from about 30,000 to about 100,000.

3. The medium of Claim 1, wherein the weight percent ratio of monomer : co-monomer can range from about 65:35 to about 90:10.

4. The medium of Claim 1, wherein the weight percent ratio of monomer : co-monomer is about 75:25.

5. The medium of Claim 1, wherein one monomer is dispersible in water and is N-vinyl-2-pyrrolidinone.

6. The medium of Claim 1, wherein one monomer is soluble in water and is selected from the group consisting of methacrylic acid, ethacrylic acid and acrylic acid.

7. The medium of Claim 1, wherein the copolymer is N-vinyl-2-pyrrolidinone-co-acrylic acid.

8. The medium of Claim 1, wherein the copolymer is used in the pigmented ink migration inhibitor in an amount of from about 1 weight percent to about 5 weight percent based on total weight of a coating solution comprising the copolymer.

9. The medium of Claim 1, wherein the copolymer is selected from the group consisting of a copolymer of N-vinylpyrrolidone, acrylic acid, and trimethoxysilylethylmethacrylate (80/10/10); a copolymer of N-vinylpyrrolidone, acrylic

acid, trimethoxysilylethylmethacrylate, and ethyleneoxide acrylate (75/10/5/10); a copolymer of N-vinylpyrrolidone, acrylic acid and N,N,N-methyloctylheptadecafluorosulfonylethylacrylate (MeFOSEA) (80/10/10); a copolymer of N-vinylpyrrolidone, acrylic acid, trimethoxysilylethylmethacrylate and N, N, N-ethyloctylheptadecafluorosulfonylethylacrylate (EtFOSEA) (83/10/2/5); and a copolymer of N-vinylpyrrolidone, acrylic acid, and Sulfonated Styrene—Sodium Salt (60/10/30).

10. The inkjet receptor medium of any of claims 1 to 9, wherein the porous membrane or porous film is selected from a microporous membrane impregnated with a microporous fluorinated silica agglomerate together with a binder and a surfactant or a combination of surfactants;
and
a microporous membrane impregnated with inorganic multivalent metal salt together with a surfactant or a combination of surfactants.

11. The inkjet receptor medium of any of claims 1 to 10, wherein the porous membrane or porous film is a Thermally Induced Phase Separated microporous membrane with tortuous paths.

12. A method of using a pigmented ink migration inhibitor, comprising the step of coating as a solution a copolymer as defined in any of Claims 1 to 9 on and into a surface of a porous membrane or film.

13. An inkjet receptor medium, comprising

(a) a porous membrane or porous film suitable for being ink jet printed with pigmented ink, and
(b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising
a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water;
wherein the porous membrane or porous film is selected from a microporous membrane impregnated with a microporous fluorinated silica agglomerate together with a binder and a surfactant or a combination of surfactants; and
a microporous membrane impregnated with inorganic multivalent metal salt together with a surfactant or combination of surfactants.

14. An inkjet receptor medium, comprising

(a) a porous membrane or porous film suitable for being ink jet printed with pigmented ink, and
(b) a pigmented ink migration inhibitor within the porous membrane or porous film, the migration inhibitor comprising
a copolymer of at least two different hydrophilic monomers, each of whose homopolymers are hydrophilic yet the resulting copolymer from the different hydrophilic monomers is sparingly soluble in water;

wherein the porous membrane or porous film is a Thermally Induced Phase Separated microporous membrane.

Patentansprüche

1. Tintenstrahlempfangsmedium, umfassend

a) eine zum Tintenstrahlbedrucken mit Pigmenttinte geeignete poröse Membran oder poröse Folie, und
b) einen Pigmenttintenmigrationsinhibitor innerhalb der porösen Membran oder porösen Folie, wobei der Migrationsinhibitor
ein Copolymer mindestens zweier verschiedener hydrophiler Monomere umfasst, wobei die jeweiligen Homopolymere hydrophil sind, das aus den verschiedenen hydrophilen Monomeren hervorgehende Copolymer jedoch in Wasser wenig löslich ist;

wobei das Zahlenmittel des Molekulargewichts des Copolymers im Bereich von 20000 bis 200000 liegt.

2. Medium nach Anspruch 1, wobei das Copolymer ein Zahlenmittel des Molekulargewichts im Bereich von etwa

30000 bis etwa 100000 aufweist.

3. Medium nach Anspruch 1, wobei das Gewichtsprozentverhältnis Monomer : Comonomer im Bereich von etwa 65: 35 bis etwa 90:10 liegen kann.

4. Medium nach Anspruch 1, wobei das Gewichtsprozentverhältnis Monomer : Comonomer etwa 75:25 beträgt.

5. Medium nach Anspruch 1, wobei ein Monomer in Wasser dispergierbar ist und N-Vinyl-2-pyrrolidinon ist.

6. Medium nach Anspruch 1, wobei ein Monomer in Wasser löslich ist und aus der Gruppe Methacrylsäure, Ethacrylsäure und Acrylsäure ausgewählt ist.

7. Medium nach Anspruch 1, wobei das Copolymer eine N-Vinyl-2-pyrrolidinon-co-acrylsäure ist.

8. Medium nach Anspruch 1, wobei das Copolymer in dem Pigmenttintenmigrationsinhibitor in einer Menge von etwa 1 Gewichtsprozent bis etwa 5 Gewichtsprozent, bezogen auf das Gesamtgewicht einer das Copolymer umfassenden Beschichtungslösung, eingesetzt wird.

9. Medium nach Anspruch 1, wobei das Copolymer aus einem Copolymer von N-Vinylpyrrolidon, Acrylsäure und Trimethoxysilylethylmethacrylat (80/10/10); einem Copolymer von N-Vinylpyrrolidon, Acrylsäure, Trimethoxysilylethylmethacrylat und Ethylenoxidacrylat (75/10/5/10); einem Copolymer von N-Vinylpyrrolidon, Acrylsäure und N, N,N-Methyloctylheptadecafluorsulfonylethylacrylat (MeFOSEA) (80/10/10); einem Copolymer von N-Vinylpyrrolidon, Acrylsäure, Trimethoxysilylethylmethacrylat und N,N,N-Ethyloctylheptadecafluorsulfonylethylacrylat (EtFOSEA) (83/10/2/5); sowie einem Copolymer von N-Vinylpyrrolidon, Acrylsäure und dem Natriumsalz von sulfoniertem Styrol (60/10/30) ausgewählt ist.

10. Tintenstrahlempfangsmedium nach einem der Ansprüche 1 bis 9, wobei die poröse Membran oder poröse Folie aus einer mit einem mikroporösen fluorierten Siliziumoxidagglomerat zusammen mit einem Bindemittel und einem grenzflächenaktiven Mittel oder einer Kombination von grenzflächenaktiven Mitteln imprägnierten mikroporösen Membran; und einer mit anorganischem mehrwertigem Metallsalz zusammen mit einem grenzflächenaktiven Mittel oder einer Kombination von grenzflächenaktiven Mitteln imprägnierten mikroporösen Membran ausgewählt ist.

11. Tintenstrahlempfangsmedium nach einem der Ansprüche 1 bis 10, wobei die poröse Membran oder poröse Folie eine mikroporöse Membran mit thermisch induzierter Phasentrennung mit gewundenen Wegverläufen ist.

12. Verfahren zur Verwendung eines Pigmenttintenmigrationsinhibitors, umfassend den Schritt Beschichten eines Copolymers wie in einem der Ansprüche 1 bis 9 definiert als Lösung auf und in eine Oberfläche einer porösen Membran oder Folie.

13. Tintenstrahlempfangsmedium, umfassend

a) eine zum Tintenstrahlbedrucken mit Pigmenttinte geeignete poröse Membran oder poröse Folie, und
b) einen Pigmenttintenmigrationsinhibitor innerhalb der porösen Membran oder porösen Folie, wobei der Migrationsinhibitor ein Copolymer mindestens zweier verschiedener hydrophiler Monomere umfasst, wobei die jeweiligen Homopolymere hydrophil sind, das aus den verschiedenen hydrophilen Monomeren hervorgehende Copolymer jedoch in Wasser wenig löslich ist;
wobei die poröse Membran oder poröse Folie aus einer mit einem mikroporösen fluorierten Siliziumoxidagglomerat zusammen mit einem Bindemittel und einem grenzflächenaktiven Mittel oder einer Kombination von grenzflächenaktiven Mitteln imprägnierten mikroporösen Membran; und
einer mit anorganischem mehrwertigem Metallsalz zusammen mit einem grenzflächenaktiven Mittel oder einer Kombination von grenzflächenaktiven Mitteln imprägnierten mikroporösen Membran ausgewählt ist.

14. Tintenstrahlempfangsmedium, umfassend

a) eine zum Tintenstrahlbedrucken mit Pigmenttinte geeignete poröse Membran oder poröse Folie, und
b) einen Pigmenttintenmigrationsinhibitor innerhalb der porösen Membran oder porösen Folie, wobei der Migrationsinhibitor ein Copolymer mindestens zweier verschiedener hydrophiler Monomere umfasst, wobei die jeweiligen Homopolymere hydrophil sind, das aus den verschiedenen hydrophilen Monomeren hervorgehende

Copolymer jedoch in Wasser wenig löslich ist;

wobei die poröse Membran oder poröse Folie eine mikroporöse Membran mit thermisch induzierter Phasentrennung ist.

Revendications

1. Support récepteur de jet d'encre, comprenant

(a) une membrane poreuse ou un film poreux approprié(e) pour être imprimé par jet d'encre avec une encre pigmentée, et
(b) un inhibiteur de migration d'encre pigmentée à l'intérieur de la membrane poreuse ou du film poreux, l'inhibiteur de migration comprenant

un copolymère d'au moins deux monomères hydrophiles différents, dont chacun des homopolymères est hydrophile, mais dont le copolymère résultant des différents monomères hydrophiles est peu soluble dans l'eau ;
dans lequel la masse moléculaire moyenne en nombre du copolymère s'échelonne de 20 000 à 200 000.

2. Support selon la revendication 1, dans lequel le copolymère a une masse moléculaire moyenne en nombre s'échelonnant d'environ 30 000 à environ 100:000.

3. Support selon la revendication 1, dans lequel le rapport des pourcentages en poids du monomère au comonomère peut s'échelonner d'environ 65:35 à environ 90:10.

4. Support selon la revendication 1, dans lequel le rapport des pourcentages en poids du monomère au comonomère est d'environ 75:25.

5. Support selon la revendication 1, dans lequel un monomère est dispersable dans l'eau et est la N-vinyl-2-pyrrolidinone.

6. Support selon la revendication 1, dans lequel un monomère est soluble dans l'eau et est choisi dans le groupe constitué par l'acide méthacrylique, l'acide éthacrylique et l'acide acrylique.

7. Support selon la revendication 1, dans lequel le copolymère est un copolymère N-vinyl-2-pyrrolidihone/ acide acrylique.

8. Support selon la revendication 1, dans lequel le copolymère est utilisé dans l'inhibiteur de migration d'encre pigmentée à raison d'environ 1 pour cent en poids à environ 5 pour cent en poids par rapport au poids total d'une solution de revêtement comprenant le copolymère.

9. Support selon la revendication 1, dans lequel le copolymère est choisi dans le groupe constitué par un copolymère de N-vinylpyrrolidone, d'acide acrylique et de méthacrylate de triméthoxysilyléthyle (80/10/10) ; un copolymère de N-vinylpyrrolidone, d'acide acrylique, de méthacrylate de triméthoxysilyléthyle et d'acrylate d'oxyde d'éthylène (75/10/5/10) ; un copolymère de N-vinylpyrrolidone, d'acide acrylique et d'acrylate de N,N,N-méthyloctylheptadécafluorosulfonyléthyle (MeFOSEA) (80/10/10) ; un copolymère de N-vinylpyrrolidone, d'acide acrylique, de méthacrylate de triméthoxysilyléthyle et d'acrylate de N,N,N-éthyloctylheptadécafluorosulfonyléthyle (MeFOSEA) (83/10/2/5) ; et un copolymère de N-vinylpyrrolidone, d'acide acrylique et de sel de sodium de styrène sulfoné (60/10/30).

10. Support récepteur de jet d'encre selon l'une quelconque des revendications 1 à 9, dans lequel la membrane poreuse ou le film poreux est choisi parmi
une membrane microporeuse imprégnée d'un agglomérat de silice fluorée microporeuse, d'un liant et d'un tensioactif ou d'une combinaison de tensioactifs ; et
une membrane microporeuse imprégnée de sel de métal multivalent minéral et d'un tensioactif ou d'une combinaison de tensioactifs.

11. Support récepteur de jet d'encre selon l'une quelconque des revendications 1 à 10, dans lequel la membrane

poreuse ou le film poreux est une membrane microporeuse à phases séparées sous l'action de la chaleur avec des trajets tortueux.

12. Procédé d'utilisation d'un inhibiteur de migration d'encre pigmentée, comprenant l'étape consistant à appliquer, en solution, un revêtement de copolymère comme défini dans l'une quelconque des revendications 1 à 9 sur et dans une surface d'une membrane poreuse ou d'un film poreux.

13. Support récepteur de jet d'encre, comprenant

(a) une membrane poreuse ou un film poreux approprié(e) pour être imprimé par jet d'encre avec une encre pigmentée, et
(b) un inhibiteur de migration d'encre pigmentée à l'intérieur de la membrane poreuse ou du film poreux, l'inhibiteur de migration comprenant

un copolymère d'au moins deux monomères hydrophiles différents, dont chacun des homopolymères est hydrophile, mais dont le copolymère résultant des différents monomères hydrophiles est peu soluble dans l'eau ;
dans lequel la membrane poreuse ou le film poreux est choisi parmi une membrane microporeuse imprégnée d'un agglomérat de silice fluorée microporeuse, d'un liant et d'un tensioactif ou d'une combinaison de tensioactifs ; et une membrane microporeuse imprégnée de sel de métal multivalent minéral et d'un tensioactif ou d'une combinaison de tensioactifs.

14. Support récepteur de jet d'encre, comprenant

(a) une membrane poreuse ou un film poreux approprié(e) pour être imprimé par jet d'encre avec une encre pigmentée, et
(b) un inhibiteur de migration d'encre pigmentée à l'intérieur de la membrane poreuse ou du film poreux, l'inhibiteur de migration comprenant

un copolymère d'au moins deux monomères hydrophiles différents, dont chacun des homopolymères est hydrophile, mais dont le copolymère résultant des différents monomères hydrophiles est peu soluble dans l'eau ;
dans lequel la membrane poreuse ou le film poreux est une membrane microporeuse à phases séparées sous l'action de la chaleur.

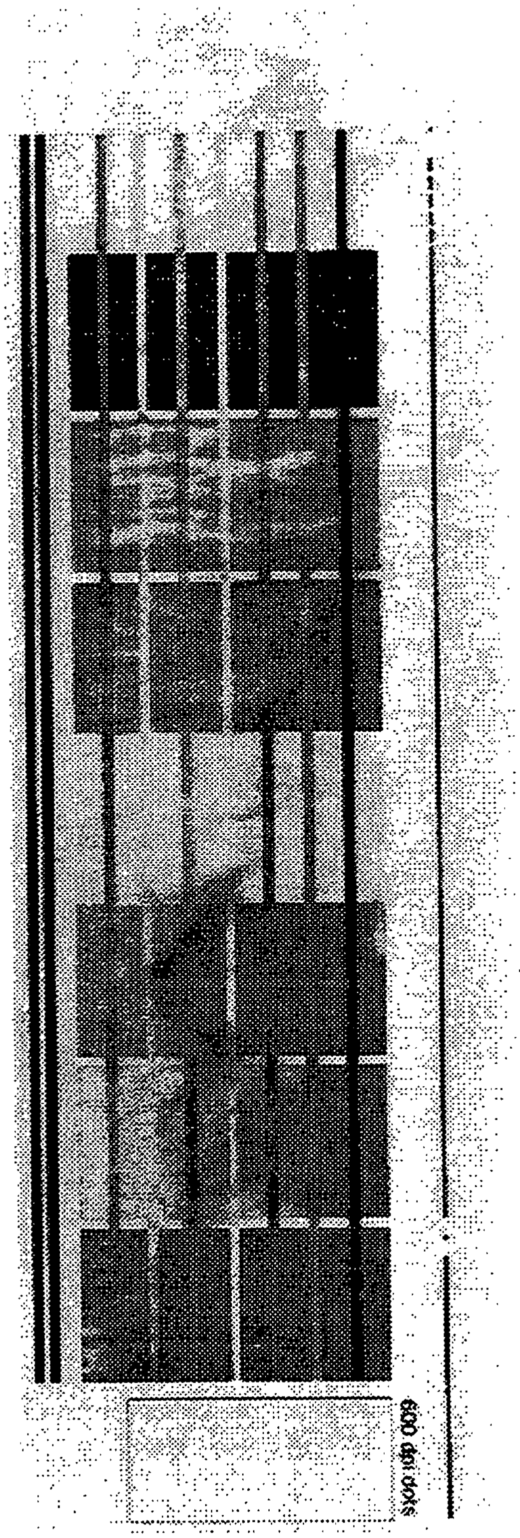


FIG. 1
Prior Art

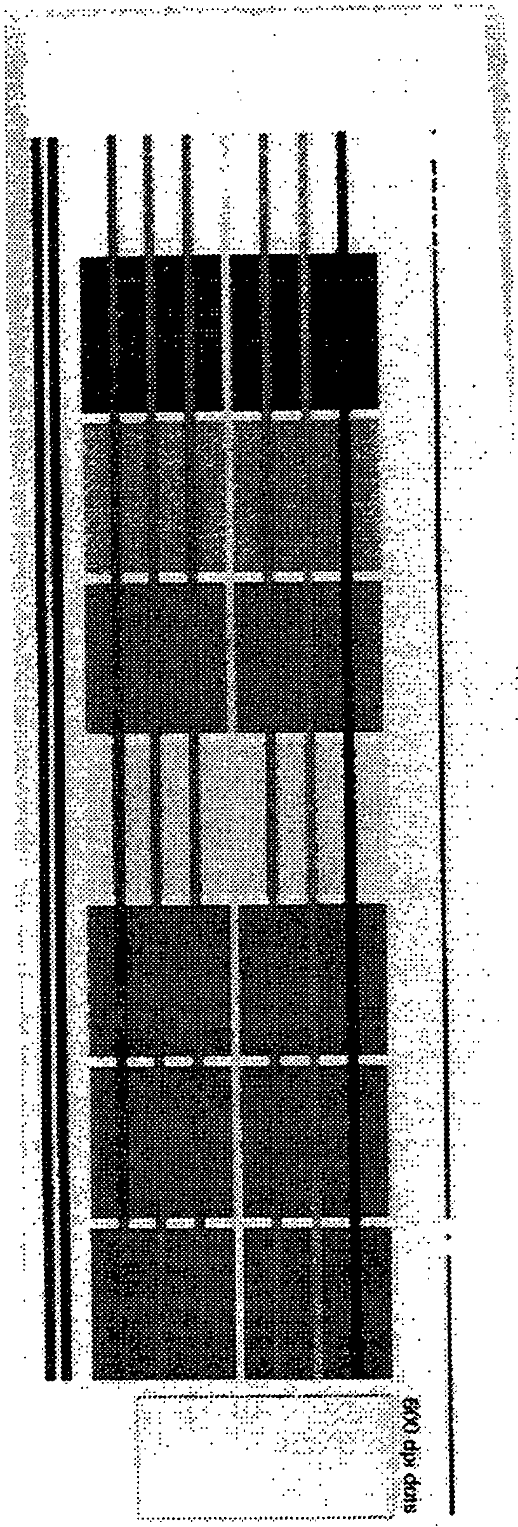


FIG. 2