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(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133–3427 (US).

(72) Inventors: FAROOQ, Omar; P.O. Box 33427, Saint Paul, MN 55133–3427 (US). WALLER, Clinton, P.; P.O. Box 33427, Saint Paul, MN 55133–3427 (US).

(74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133–3427 (US).

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(54) Title: INKJET RECEPTOR MEDIA COMPRISING METALLIC SALTS

(57) Abstract

Metallic salts useful for inkjet receptor media are disclosed. The metallic salt can be a multivalent metal derivative of an aromatic carboxylic, sulfocarboxylic, sulfophenolic, or combination thereof. The aromatic moiety can be a simple aromatic, a condensed aromatic, a heterocyclic aromatic or a combination thereof. The multivalent metal ion can be derived from the group IIA to VIA and Group IB to VIIIB of elements in the Periodic Table. The metallic salt simultaneously releases the multivalent metal cation and the organic acid anion for both pigment management and ink–drying.

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INKJET RECEPTOR MEDIA COMPRISING METALLIC SALTS

Field of Invention

This invention relates to the use of organometallic salts for pigment management in microporous inkjet receptor media.

Background of Invention

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.

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.

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.

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.

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).

Porous membrane is a natural choice to use as a 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 is 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 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.

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.

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.

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.

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.

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.

European Patent Publication EP 0 716 931 Al 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 is long term storage without fading from heat or light.

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.

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.

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. No. 5,747,148 (Warner 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.

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.

Summary of Invention

In the present work, an organometallic salt improves on the art by rapidly releasing multivalent metal cation which takes care of the pigment management function and an organic anion which provides useful organic acid to control smudgeness and drying of the film. This work, therefore, solves the need for an inkjet receptor to have both a pigment management system for flocculating or agglomerating of incoming ink and a drying agent for the humectants of the ink thus efficiently drying the pigmented inks within a porous substrate.

One aspect of the invention is an inkjet receptor medium, comprising a composition of matter comprised of an organometallic salt of a multivalent metal cation and an organic acid anion.

One aspect of the present invention is to provide a metal salt that releases a metal cation for pigment management and simultaneously releases an organic acid anion of a carboxylic or sulfocarboxylic or phenolic acid or hydroxy or mixed functionalities thereof to take care of the drying aspect of the ink system.

"Drying agent" means an agent, component, ingredient or compound which can dry or make the pigment feel dry to touch via chemically or physicochemically occlusion or interaction with certain components such as the humectant or other slow drying components in the pigmented inks used in printing the image onto the receptor medium. Specifically, "dry to touch" means, an indistinguishable "feel" between the imaged and the unimaged areas of the substrate regardless of whether, technically, all volatiles have evaporated from the imaged area.

One feature of the present invention is a multivalent organometallic salt that releases a multivalent metal ion for pigment management and an anion of an organic acid consisting of a carboxylic and/or a sulfonic acid or hydroxyl or a phenolic or a mixed functionality thereof in a composition in an aqueous solution wherein the acid works as an ink-drying agent in a film coated with the said composition.

One advantage of the present invention is that both the multivalent metal cation and the organic acid can be derived from the same salt/component. This advantage avoids the necessity of providing two different components to a porous substrate. Furthermore, the procedure minimizes the possibility that the coating solutions become contaminated with any undesirable residue or components or by product-compounds as contaminants.

Another feature of the present invention is that a composition including the organometallic salt, surfactant and the migration inhibitor uses a lesser amount of total solids to achieve comparable performance. Thus, one can minimize concentration to obtain equivalent performance or maximize concentration to achieve previously-unattainable performance.

Other features and advantages of the invention will be disclosed in relation to the embodiments of the invention.

Embodiments of Invention

Inkjet Receptor Medium

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.

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.

Another embodiment of that medium 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 said 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.

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.

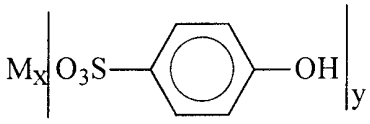
One embodiment of the present invention is an inkjet receptor comprising a microporous membrane impregnated with an organometallic multivalent salt together with a hydrophilic surfactant and an optional migration inhibitor polymer/copolymer chosen from a series of hydrophilic/hydrophobic polymers/copolymers.

Another embodiment of the present invention is an inkjet medium comprising a microporous membrane impregnated with an organometallic multivalent salt wherein the said salts are derived from various aromatic acids consisting of sulfonic, carboxylic, phenolic, hydroxyl and mixed functionalities thereof and wherein the metal ions may be derived from group IIA to VIA and more preferably from group IB to VIIIB in the Periodic Table. Specific

examples, include, but are not limited to, Al, Mg, Zn, Fe, Bi, Ga, Sn, Ca,, Ti, Zr, Cu, Co etc.

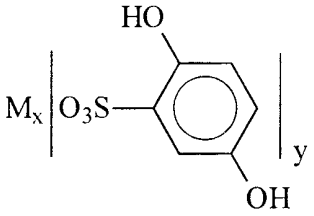
Nonlimiting examples of organometallic salts useful in the present invention include: .

Metal Sulfocarbolates



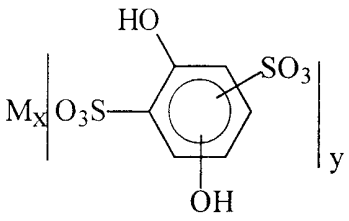
M = Cu, Mg, Co (x:y = 1:2); M = Al, Ga (x:y = 1:3, 2:3)

Metal Hydroquinonesulfonates



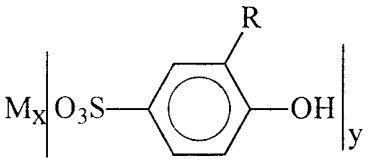
M = Cu, Mg, Co (x:y = 1:2, 2:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:3, 2:2)

Metal dihydroxybenzenedisulfonates



M = Cu, Mg, Co (x:y = 1:1, 1:2) ; M = Al, Ga, Ti, Zr (x:y = 1:1, 2:2, 4:3)

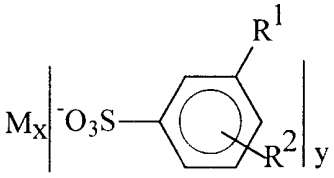
Metal Sulfosalicylates



M = Cu, Mg, Co (x:y = 1:2, 1:1); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:3, 3:3)

R = -COOH (Li^+, Na^+, K^+)

Metal Sulfophthalates

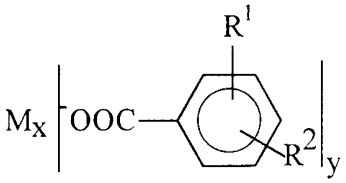


M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)

$R^1 = R^2$ = -COOH (Li^+, Na^+, K^+)

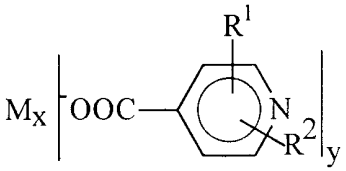
Metal Carboxylates

(a)



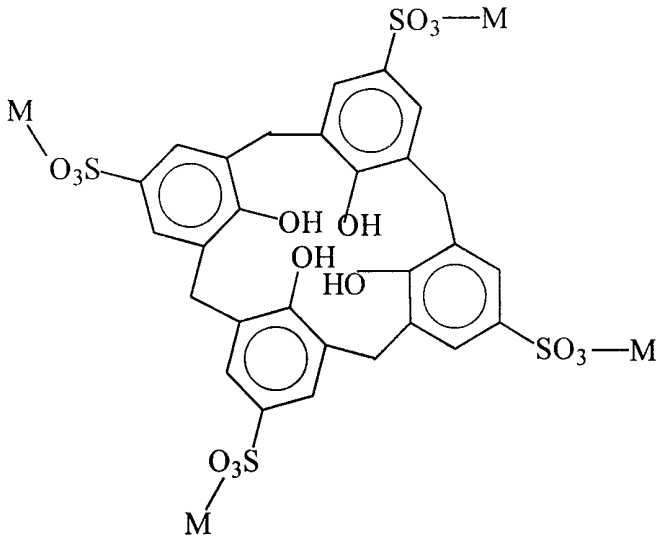
M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)
R^1 = -COOH (Li^+, Na^+, K^+), R^2 = -OH

(b)



M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)
R^1 = -COOH (Li^+, Na^+, K^+), R^2 = -OH

Metal Calix(n) arene sulfonates



M = Cu, Mg, Co, Ca, Al, Ti, Zr, Zn etc.
n = 4-8

Another embodiment of the present invention is an inkjet medium

comprising a microporous membrane impregnated with an organometallic multivalent salt wherein the said salt releases both a multivalent metal cation and an organic acid anion and wherein the metal cation plays the role of pigment management system and the organic acid anion plays the role of a dehydrating or drying agent thus making the image in the membrane smudge-free to touch.

Another embodiment of the present invention is an inkjet medium comprising a microporous membrane impregnated with an organometallic multivalent salt wherein the said salt releases both a multivalent metal cation and an organic acid anion - both simultaneously being useful for pigment management system and humectant management system in the ink.

Another embodiment of the present invention is an inkjet coating composition that incorporates an organometallic multivalent salt with a surfactant and a binder only to give a composition which provides 0.33 to 0.25 of the coating weight of that a composition consisting of an inorganic salt, a surfactant, organic acid and a binder.

The ink colorant is typically a pigment dispersion having a dispersant that binds to the pigment that will destabilize, flocculate, agglomerate, or coagulate the pigments on contact with the media component. Depositing each of 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.

More preferably, the inkjet receptor medium uses a Thermally Induced Phase Separated (T.I.P.S.) microporous membrane 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), 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: drop volume, porosity of media, and capacity of media to receive ink. 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.

Optional Additives

Pigment Drying agents

Pigment drying agents can be useful in the present invention and can comprise aromatic or aliphatic acids having sulfonic, carboxylic, phenolic or mixed functionalities thereof.

Preferably, aromatic sulfonic and carboxylic acids have been found in this invention to be very effective in presence of multivalent metal salts and suitable surfactant and binder, to serve as drying agents for inkjet receptor media. These acids can be of various types, chosen according to properties and distinguished by extent of their solubility in water and how that solubility affects drying performance.

At one end of the range of candidate acids, their higher solubility in water can interfere with other components in the media, such as a migration inhibitor thereby perhaps requiring a greater concentration of drying agent to be included in the coating. One example of this type of acid is a sulfocarboxylic acid such as sulfosalicylic acid.

At the other end of the range of candidate acids, the candidate acids with lower solubility in water would perform the drying function excellently but could require more aggressive solvent(s) to be impregnated into the media. One example of this type of acid is a phthalic acid so long as it is recognized that impregnating the receptor media will be more challenging because of the acid's lower solubility. To overcome impregnating limitations, lower solubility acid candidates, such as aromatic carboxylic acids, can be derivatized to become a monosodium salt (or any other similar alkali metal salt), the solubility of that salt in water is enhanced. One example of this type of acid-salt is an aromatic

carboxylic acid, sodium salt such as *ortho*-phthalic acid-sodium salt. Furthermore, the aromatic carboxylic acids are also sufficiently soluble in water when the aromatic moiety contains at least one sulfonic acid group attached to the aromatic ring either as acid or as its sodium salt (or other alkali metal salts). Two examples of these candidates are 5-sulfoisophthalic acid and also its monosodium salt.

Other functional groups such as --OH group can be attached to the aromatic moiety to increase the solubility of the aromatic carboxylic group. Examples in this category are hydroxy-aryldicarboxylic acid isomers.

A related factor to choice of lower water solubility candidate acid is the amount of the acid to be included in the receptor media. The relationship is generally such that the lower solubility acid candidates are needed in smaller amounts than the higher solubility acid candidates. Generally, an acid used in the present invention can be present in the receptor medium in an amount ranging from about 1 to about 20 weight percent of the total coating weight of compositions with which the medium is impregnated with a fluid management system/pigment management system. Preferably, the amount ranges from about 4 to about 15 weight percent. Thus, a sodium salt of an aromatic sulfocarboxylic acid should be present in an amount in the higher end of the range (e.g., about 15 weight percent), whereas a carboxylic acid should be present in an amount in the lower end of the range (e.g., about 5 weight percent).

Moreover, free acid and salt forms of that acid can be combined for controlled tailoring of impregnation processing and resulting drying performance.

The acid or its salt can be impregnated into the media by adding it to a coating solution otherwise being impregnated into the media for fluid management and pigment management purposes. Suitable coating solutions comprise a multivalent inorganic salt, a suitable surfactant, an alcohol and water. The weight percent of the acid/salt being used usually ranges from about 40 to about 60 weight percent and more preferably from about 45 to about 55 weight percent of the total solids in the composition.

Pigment Migration Inhibitors

Pigment migration inhibitors can be used in the present invention as an optional additive. These inhibitors 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.

Nonlimiting examples of hydrophilic monomers are methacrylic, ethacrylic acids, acrylic acid, N-Vinylphthalimide, Vinylimidazole, Vinylpyridine and N-vinyl-2-pyrrolidinone, with the last and acrylic acid being presently preferred. The homopolymer is a polyvinylpyrrolidinone (PVP) of relatively high molecular weight available from commercial sources.

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 (MeFOSEA) (83/10/2/5); and); a copolymer of N-vinylpyrrolidone, acrylic acid, and Sulfonated Styrene--Sodium Salt (60/10/30).

Usefulness of the Invention and Examples

It has been found that ink migration of the pigment particles can occur when capillary forces cause pigment particles of a portion of a printed inkjet medium is partially submerged in water. Only the area of printed ink above migrates, and typically only after several hours of submersion of the other portion of the printed ink. This noticeable ink migration is in a manner like thin layer chromatography.

It has also been found that ink migration of the pigment particles can occur when an overlaminate is used over the printed ink to protect the image. However, at the edge of the overlaminate and the printed ink, water can ingress and cause capillary movement of the pigment underneath the overlaminate.

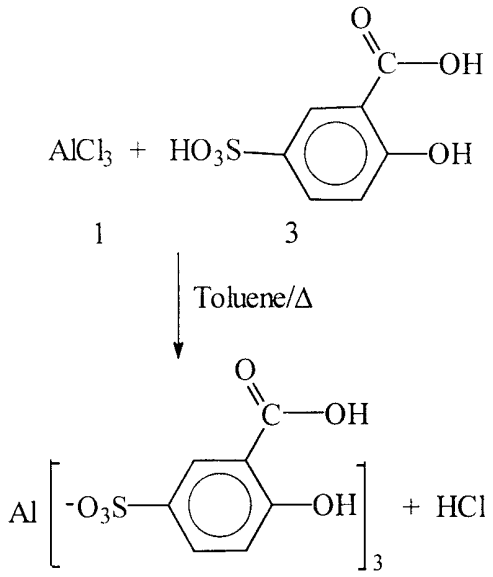
In the present invention the complexation of multivalent metal cation with the chemically released organic acid anions and the migration inhibitor provides not only efficient pigment and humectant management systems but also allows significant pigment inhibition on the film that it is found to be completely water-fast within 2 minutes to 2 hrs of imaging without mechanical rubbing.

The following examples illustrate the invention in more detail.

Reaction of polyfunctional aromatic compounds containing sulfonic, carboxylic, hydroxyl groups and mixed groups thereof with certain metal halides, pseudo-halides and alkoxides lead to several classes of novel organometallic salts. These salts have been prepared according to the following procedure.

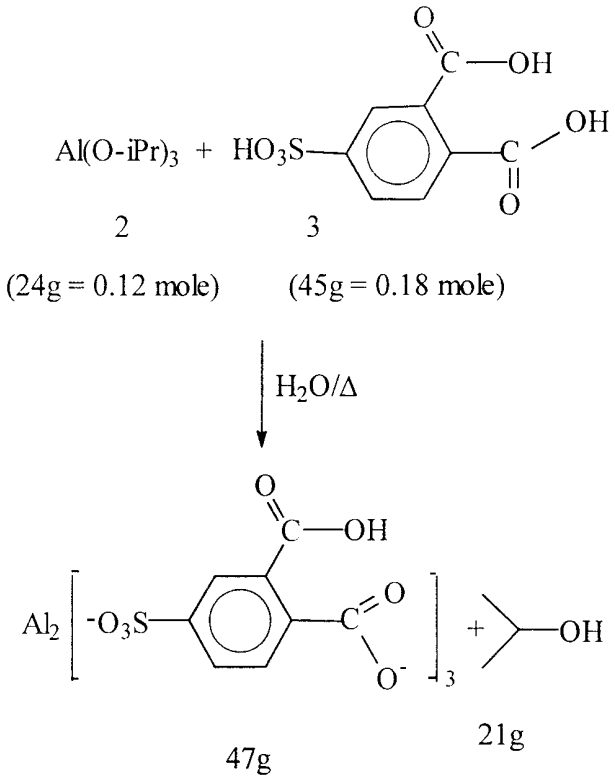
Example-1:

Various classes of organometallic salts were prepared by refluxing appropriate quantities of metal chlorides and hydroxysulfonic acids in toluene for 8-9 hrs. The materials were filtered, dried in air and stored. In a typical experiment, to a solution of 90g of 5-sulfosalicylic acid (0.35 mole) in 100g toluene was added 15.7g (0.12 mole) of aluminum chloride and the mixture was heated to near-reflux temperature of the solvent for about 8 hrs. The white solid precipitated was filtered and dried. The product was characterized by the usual analytical techniques.



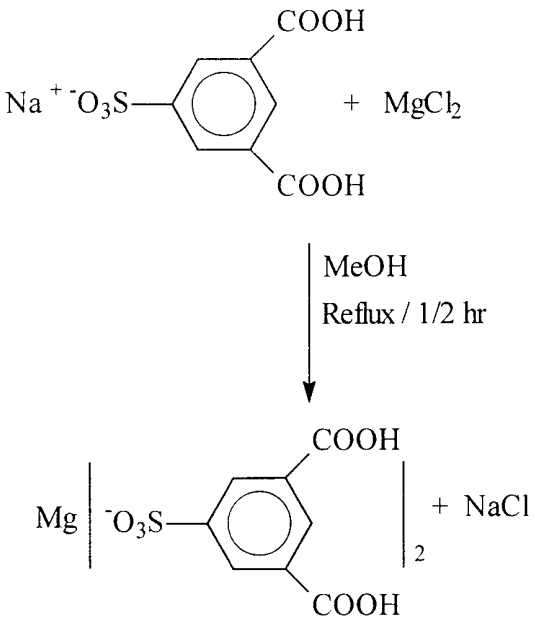
Example-2:

The same classes of materials were also prepared by using appropriate metal alkoxides and hydroxysulfonic or sulfocarboxylic acids in water. Thus, aluminum isopropoxide was mixed with 5-sulfophthalic acid in 2:3 molar ratio and the mixture was heated to about 60^0C for about ½ hr. Aluminum isopropoxide was hydrolyzed and the salt was obtained as aqueous solution and was used as such for inkjet coatings. Magnesium ethoxide was similarly hydrolyzed from its mixture with the same acid in 1:2 molar ratio to obtain magnesium sulfophthalate in aqueous solution.



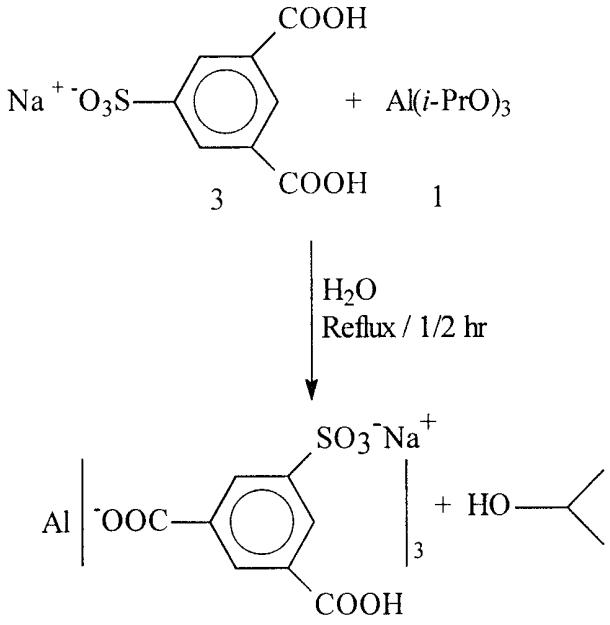
Example-3:

The same class of salts were also prepared by yet another procedure *Viz.* metathetical ion-exchange. Thus, a solution of 5-sulfoisophthalic acid-Na salt (20 g, 0.075 mole) in methanol was mixed with magnesium chloride (3.5 g, 0.0375 mole), and the mixture was refluxed for about ½ hr. The solution was concentrated and sodium chloride was crystallized out. The solution was decanted to obtain 5-sulfoisophthalic acid-Mg salt in solution.



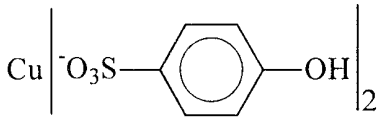
Example-4:

Carboxy-derivative of the class of materials were prepared by hydrolyzing metal alkoxide with aromatic carboxylic acid or functionalized aromatic carboxylic acids. Thus, refluxing a mixture of 24g (0.090 mole) 5-sulfoisophthalic acid-Na salt with 6.1g (0.030 mole) aluminum isopropoxide in 3:1 molar ratio in aqueous media for about ½ hr, aluminum tris(5-sulfoisophthalate-Na salt) was obtained in solution.



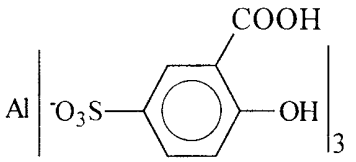
Example-5:

The following organometallic salts (I-IV) were used in the following compositions. The compositions were coated onto oil-in microporous polypropylene membrane prepared by the 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). The impregnated membrane was dried and then imaged in an HP-2500 series wide-format inkjet printers (Hewlett Packard Corporation of Palo Alto, CA, USA) to obtain instantaneously dry, smudge-free and water-fast images.



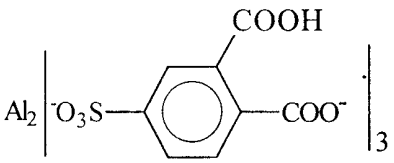
Copper(II)sulfocarbolate

I



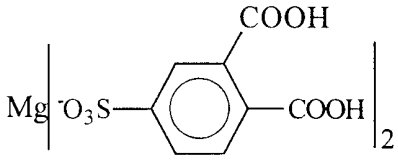
Aluminum 5-sulfosalicylate

II



Aluminum 5-sulfophthalate

III



Magnesium 5-sulfophthalate

IV

Composition-I:

Aluminum 4-sulfophthalate - III	7.0%
Dioctylsulfosuccinate (Dos[3])	5.0%NVP/AA (copolymer) 2%
IPA	25%
De-ionized water	61%

Composition-II:

Copper(II)sulfocarbolate - I	5.2%
Aluminum sulfate (octadecahydrate)	4.1%
Dioctylsulfosuccinate (Dos[3])	7.0%
NVP/AA (copolymer)	2.0%
IPA	25%
De-ionized water	45%

Composition-III:

Aluminum 5-sulfosalicylate - II	7.0%
Dioctylsulfosuccinate (Dos^3)	6.0%
NVP/AA (copolymer)	2%
IPA	25%
De-ionized water	60%

Composition-IV:

Magnesium 5-sulfophthalate - IV	5.3%
Dioctylsulfosuccinate (Dos^3)	6.0%
NVP/AA (copolymer)	2%
IPA	25%
De-ionized water	60%

The described compositions were coated onto a 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) that 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 96 hours. During this time of submersion, the image did not show any deterioration due to pigment migration.

The above described examples were repeated successfully using yet another 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/cm2
Caliper	0.178 mm (7 mil)

The film was dried at about 76°C-121°C within 1-2 minutes. The impregnated membrane when imaged in HP-2500 series printer provided very high quality and high-density image which was instantaneously dry, tack-free, feathering-free, and smudge-free. The image did not show any movement in any of the ink/color on water-challenging done in the same manner as disclosed above in the prior example.

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

What is claimed is:

1. An inkjet receptor medium, comprising a composition of matter comprised of an organometallic salt of a multivalent metal cation and an organic acid anion.

2. The medium of claim 1 wherein the multivalent metal cation is derived from group IIA to VIA and group IB to VIIIB in the Periodic Table having capability of forming organometallic salts/compounds with the organic acid anion.

3. The medium of claim 1, wherein the organic acid anion is selected from the group consisting of acids having a carboxylic, sulfonic, phenolic and mixed functionalities thereof and wherein the organic acid anion is an aromatic acid.

4. The medium of claim 3, wherein the aromatic acid comprises a sulfocarboxylic acid, a sulfosalicycylic acid, or a sulfophenolic acid.

5. The medium of claim 1 wherein the said organometallic salts are derived from the reaction of a metal halide or a pseudo-halide with an organic acid

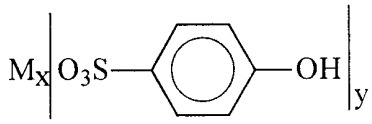
6. The medium of claim 1 wherein the organometallic salts are derived from the reaction of a metal alkoxide with an organic acid via simple hydrolysis in an aqueous medium.

7. The medium of claim 1 wherein the organometallic salt comprises any of monomeric, dimeric, trimeric salts whose solubility is dictated by the degree of complexation.

8. The medium of claim 1, further comprising a porous substrate into which the organometallic salt is impregnated together with a surfactant.

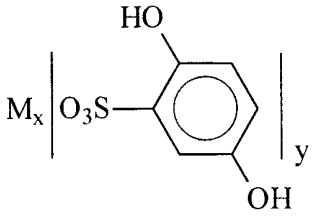
9. The medium of claim 8, wherein the porous substrate is a microporous polypropylene membrane.

10. The medium of claim 1, wherein the organometallic salt is a metal sulfocarbolate of the formula:



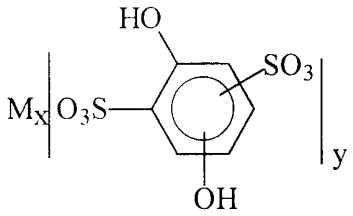
M = Cu, Mg, Co (x:y = 1:2); M = Al, Ga (x:y = 1:3, 2:3)

11. The medium of claim 1, wherein the organometallic salt is a metal hydroquinonesulfonate of the formula:



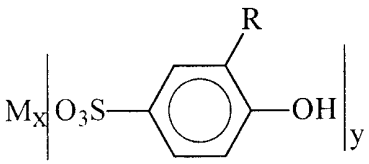
M = Cu, Mg, Co (x:y = 1:2, 2:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:3, 2:2)

12. The medium of claim 1, wherein the organometallic salt is a metal dihydroxybenzenedisulfonate of the formula:



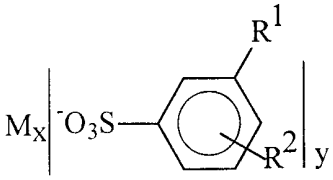
M = Cu, Mg, Co (x:y = 1:1, 1:2) ; M = Al, Ga, Ti, Zr (x:y = 1:1, 2:2, 4:3)

13. The medium of claim 1, wherein the organometallic salt is a metal sulfosalicylate of the formula:



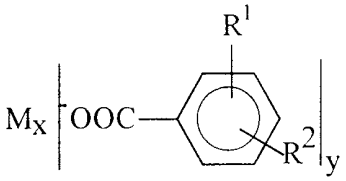
M = Cu, Mg, Co (x:y = 1:2, 1:1); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:3, 3:3)
R = -COOH (Li^+, Na^+, K^+)

14. The medium of claim 1, wherein the organometallic salt is a metal sulfophthalate of the formula:



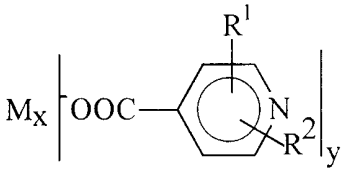
M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)
$R^1 = R^2$ = -COOH (Li^+, Na^+, K^+)

15. The medium of claim 1, wherein the organometallic salt is a metal carboxylate of the formulae:



M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)

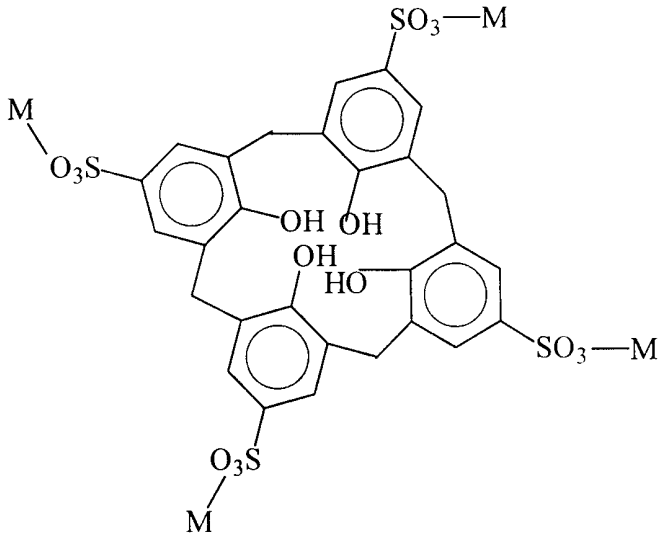
R^1 = -COOH (Li^+, Na^+, K^+), R^2 = -OH



M = Cu, Mg, Co (x:y = 1:1, 2:2, 3:2); M = Al, Ga, Ti, Zr (x:y = 1:3, 2:2, 2:3)

R^1 = -COOH (Li^+, Na^+, K^+), R^2 = -OH

16. The medium of claim 1, wherein the organometallic salt is a metal Calix(n)arene sulfonate of the formula:



M = Cu, Mg, Co, Ca, Al, Ti, Zr, Zn etc.

n = 4-8

17. A method of imaging a graphic on a porous substrate, comprising the steps of:

(a) impregnating an organometallic salt of claim 1 in the porous substrate; and

(b) delivering ink to the porous substrate.

18. The method of claim 17, wherein the impregnating step (a) also includes impregnating a surfactant and a Migration inhibitor.

19. An image graphic, comprising ink in and on a porous substrate, wherein the porous substrate contains an organometallic salt of claim 1 and wherein the ink interacts with the organometallic salt in a complexation of metal cation of the salt with dispersant in the ink.

INTERNATIONAL SEARCH REPORT

Interr .al Application No
PCT/US 99/03472

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00 C07C309/60 C07C309/58 C07C309/42

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)
IPC 6 B41M C07C

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 practical, 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.
X	EP 0 661 168 A (CANON KK) 5 July 1995 see page 4, line 41 - line 44 see page 5, line 26 - line 34 see page 6, line 6 - line 13 see page 8, line 25 - line 29 see page 10, line 43 - line 44 see examples 45-50 -----	1-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 June 1999	16/06/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Markham, R

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INTERNATIONAL SEARCH REPORT

...ormation on patent family members

Intern... al Application No
PCT/US 99/03472

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP 8025794 A	30-01-1996
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		AU 687121 B	19-02-1998
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