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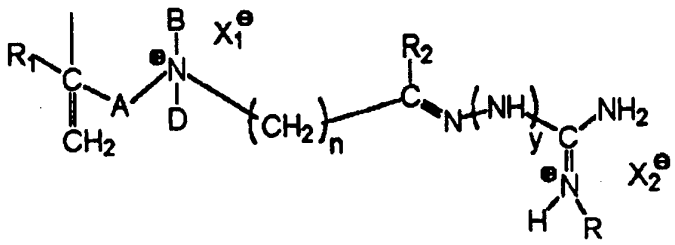

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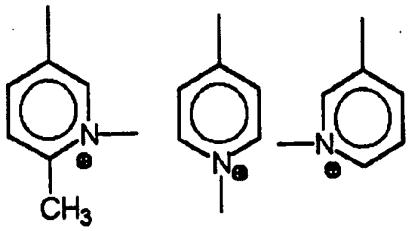

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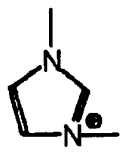

(III)

(57) Abstract

An improved ink-receptive sheet comprising a transparent substrate bearing on at least one major surface, an ink-receptive layer comprising an imaging copolymer comprising at least one monomer having quanidinyl functionality (I) wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, -COO-(CH_2CH_2O)n-CH_2-,-CONH-(CH_2CHO)n-CH_2-, and -(CH_2-CH_2-NH_2C1)n-, wherein n is from about 1 to about 5; B and D are separately selected from the group consisting of alkyl group having from about 1 to about 3 carbon atoms; or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of (II) and (III); R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms; R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms, y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions.

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IMPROVED INK-RECEPTIVE SHEET

Background of the Invention

Field of the Invention

The invention relates to transparent materials that can be used as ink-receptive sheets for imaging, and more particularly, to improved ink-receptive layers therefor, such materials having improved shelf life after imaging.

Description of the Related Art

Imaging devices such as ink jet printers and pen plotters are now commonly used for printing various information including labels and multi-color graphics. Presentation of such information has created a demand for transparent imageable ink receptive sheets that can be used as overlays in technical drawings and as transparencies for overhead projection.

Imaging with either the ink jet printer or the pen plotter involves depositing ink on the surface of these transparent receptors. These imaging devices conventionally utilize inks that can remain exposed to air for long periods of time without drying out.

Since it is desirable that the surface of these receptors be dry and non-tacky to the touch soon after imaging, even after absorption of significant amounts of liquid, transparent materials that are capable of absorbing significant amounts of liquid while maintaining some degree of durability and transparency are very desirable as imageable receptors for imaging.

Compositions useful as transparent liquid-absorbent receptors have been formed by blending and coating a liquid-soluble polymeric material with a liquid-insoluble polymeric material. The liquid-insoluble materials are presumed to form a matrix, within which the liquid-soluble

materials reside. Examples of such blends are disclosed in U.S Patents Nos. 4,300,820, 4,369,229, and 4,935,307.

A problem in using the various blends of liquid-absorbent polymers is the basic incompatibility of the matrix-forming insoluble polymer with the liquid being absorbed. This can inhibit the absorption capability of to some extent and may increase the drying time.

Liquid-absorbent materials disclosed in U.S. Patent Nos. 5,134,198, 5,192,617, 5,219,928 and 5,241,006 attempt to improve drying and decrease dry time. These materials comprise crosslinked polymeric compositions capable of forming continuous matrices for liquid absorbent semi-interpenetrating polymer networks. These networks are blends of polymers wherein at least one of the polymeric components is crosslinked after blending to form a continuous network throughout the bulk of the material, and through which the uncrosslinked polymeric component(s) intertwine to form a macroscopically homogenous composition. Such compositions are useful for forming durable, ink absorbent, transparent graphical materials without the disadvantages of the materials listed above.

Generation of an image by an ink jet printer results in large quantities of solvent, generally blends of glycols and water, which remain in the imaged areas. Diffusion of this solvent into unimaged areas can result in "bleeding" of the image, when the dye is carried along with the solvent.

Materials disclosed in the above references do not address this effect, which is exacerbated in transparency materials. This exacerbation occurs when the imaged films are stored at elevated temperatures and high humidity conditions, or when the solvent is otherwise prevented from leaving the film, e.g., when the imaged film is placed in a transparency protector. Since the majority of the solvent is generally absorbed and not evaporated, and the absorbent coatings are usually very thin, providing more chances for lateral diffusion, the bleeding effect

becomes more severe upon aging or archiving in such protectors.

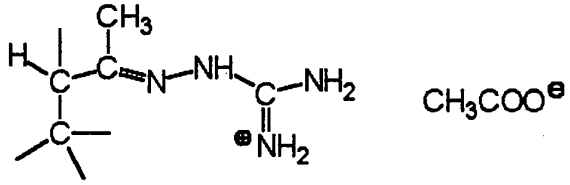
Japanese patent publication 63-307979 teaches the use of certain quaternary ammonium containing polymer mordants in an ink jet film and claims to show no running or spreading of ink during the ink jet recording process, thereby giving good initial resolution, high density, good color reproduction and lustre. However, no mention is made of preventing bleeding upon aging or archiving.

The present inventors have now discovered a transparent ink-receptive material, which when used as an ink receptive layer in an ink receptive sheet or transparency, yields improved shelf life after imaging. Even after the imaged film is exposed to elevated temperature and high humidity, and also when stored in a transparency protector, bleeding is dramatically reduced.

Other Art

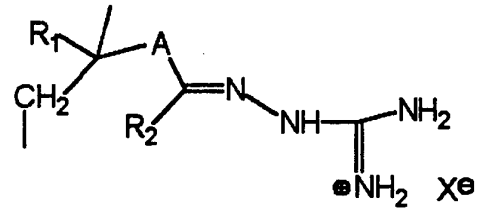
Polymeric mordants are well known in the photographic sciences and normally comprise materials containing quaternary ammonium groups, or less frequently phosphonium groups.

U.S. 2,945,006 comprises mordants which are reaction products of aminoguanidine and carbonyl groups, having the following generic formula:



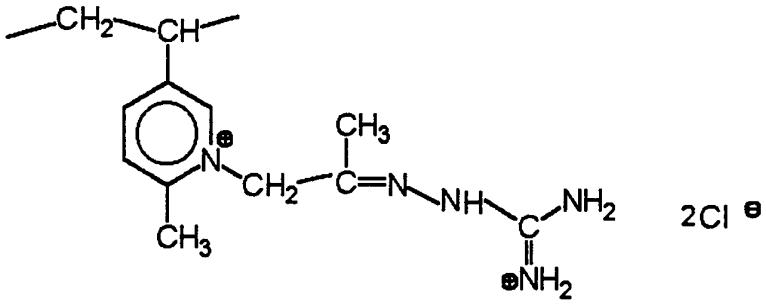
U.S. Patent No. 4,695,531 discloses mordants in a light-sensitive silver halide element for radiographic use. A spectrally sensitized silver halide emulsion layer is coated on at least one side of a transparent base, and coated between the base and the silver halide emulsion layer is a hydrophilic colloid layer containing a water-soluble acid dye capable of being decolorized during the

photographic process. This dye is associated with a basic polymeric mordant comprising the following repeating unit:



wherein R1 is hydrogen or a methyl group, A is a -COO- or -COO-alkylene group, R2 is hydrogen or a lower alkyl group, and X is an anion. There is no mention of using such mordants in an ink receptive layer.

Another photographic mordant is disclosed in an Italian Patent No. 931,270 having the following structure:



There is no mention of use in an ink receptive layer.

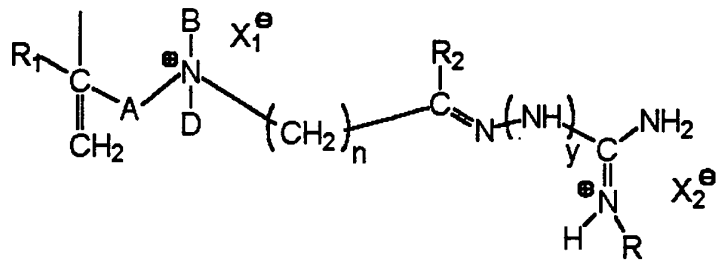
Non-diffusive mordants based on poly(N-vinylimidazole) are disclosed in U.S Patent No. 4,500,631. These are used in radiographic image-forming processes where the mordants are coupled with water-soluble dyes. Again, there is no mention of use in ink-receptive coatings.

Summary of the Invention

The invention provides an improved ink-receptive layer, and ink-receptive sheets having an improved ink-receptive layer, which exhibits longer imaged shelf life, even when exposed to elevated temperatures and humidity. The sheets of the invention show a marked reduction in ink "bleeding" and thus remain useful over a long period of

time. The sheets even show an improved life when stored in a transparent film "sleeve" protector.

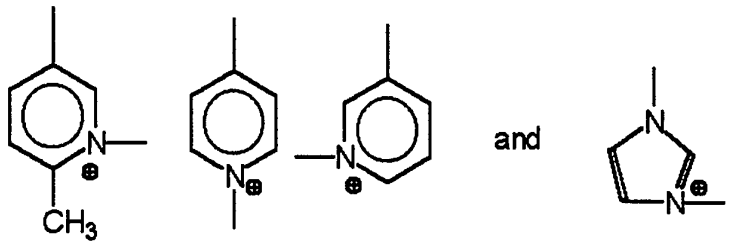
The improved ink-receptive sheets of the invention comprise a substrate bearing on at least one major surface thereof, an ink-receptive layer comprising an imaging copolymer. The imaging copolymer is formed from monomers including at least one mordanting monomer having a guanidinyl functionality of the following general structure:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 33 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and

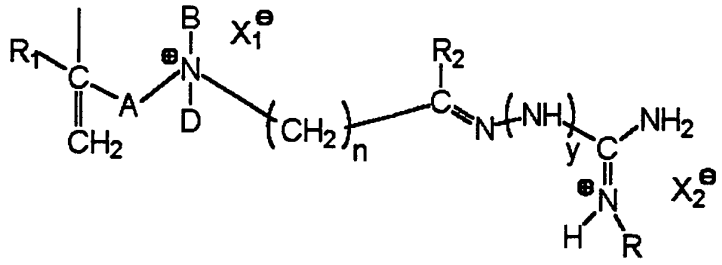
X_1 and X_2 are anions.

Preferably, the improved ink-receptive sheets of the invention comprise a transparent substrate bearing on at least one major surface thereof, an ink-receptive layer comprising an imaging copolymer, said imaging copolymer being formed from monomers comprising

a) at least one nitrogen-containing hydrophilic and water absorptive monomer selected from the group consisting of vinyl lactams such as N-vinyl-2-pyrrolidone; acrylamide, methacrylamide and their N-monoalkyl and N,N-dialkyl derivatives thereof; alkyltertiaryaminoalkylacryates and methacrylates; and vinylpyridines such as 2-vinyl and 4-vinyl pyridines;

b) at least one hydrophilic monomer selected from the group consisting of hydroxyalkyl acrylate and methacrylate, alkoxyalkyl acrylate and methacrylate, said alkyl group having from 1 to 5 carbon atoms;

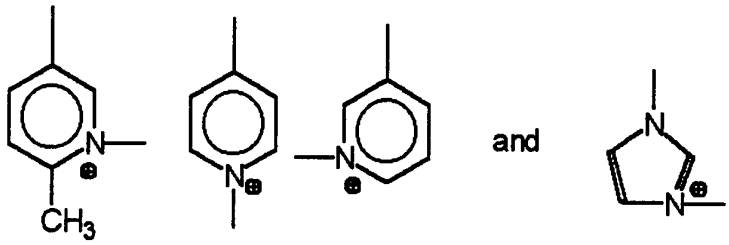
c) at least one mordanting monomer comprising a guanidinyl functionality of the following general structure:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 5 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CH_2O)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 5 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 5 carbon atoms,

y is selected from the group consisting of 0 and 1, and

X_1 and X_2 are anions.

More preferably, the ink-receptive layer comprises a crosslinked semi-interpenetrating network, hereinafter referred to as an SIPN, formed from:

a) at least one crosslinkable polymeric component,

b) at least one liquid-absorbent polymeric component comprising a water-absorbent polymer,

c) at least one mordanting monomer, and

d) optionally, a crosslinking agent.

The SIPNs are continuous networks wherein the crosslinked polymer forms a continuous matrix. The SIPN is a network comprising a crosslinkable component containing from about 0.5 to about 20% ammonium acrylate groups, a crosslinking agent, with a liquid absorbent polymeric component, and a mordanting monomer having properties described, supra.

This invention provides an ink-receptive sheet useful for projecting an image, commonly called a "transparency" which, when imaged with an ink depositing device has reduced image bleeding, and improved shelf life, even when it is exposed to elevated temperature and high humidity, or in cases where solvent is prevented from leaving the coating, e.g., when stored in a transparency protector.

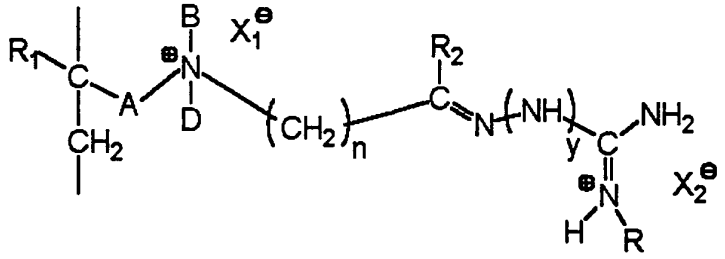
In a highly preferred embodiment, the ink-receptive sheets of the invention comprise a transparent substrate bearing on at least one major surface thereof an ink-receptive layer comprising:

a) at least one crosslinkable polymeric component formed from monomers comprising:

1) at least one hydrophilic nitrogen-containing monomer,

2) at least one ethylenically α,β-unsaturated monomer, and

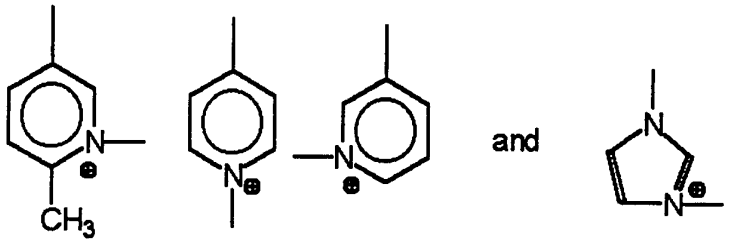
3) at least one mordanting monomer comprising a guanidinyl functionality having the following general structure:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 3 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions;

b) at least one liquid-absorbent polymeric component,

c) a polyfunctional aziridine crosslinking agent, and

d) a particulate material having a particle size distribution ranging from the about 5 μm to about 40 μm.

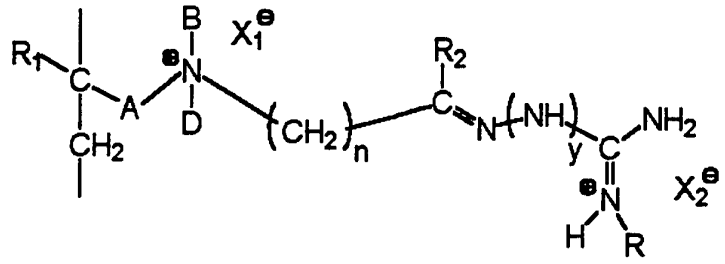
In another embodiment of the invention, the image recording sheet comprises a substrate bearing on at least one major surface a two-layer composite medium for sorbing liquids comprising:

a) a liquid-sorbent underlayer comprising an imaging copolymer, and, overlying said underlayer,

b) a liquid-permeable surface layer,

the liquid sorbtivity of said underlayer being greater then the liquid sorptivity of said surface layer whereby the composite medium has a sorption time less than the sorption time of a thickness of said surface layer equal to the thickness of the composite medium, wherein at least one layer comprises a copolymer formed from monomers comprising at least one mordanting monomer having a

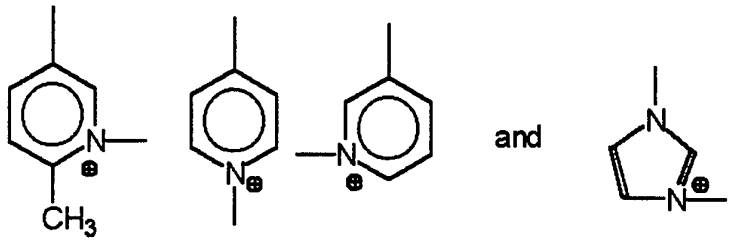
guanidinyl functionality of the following general formula:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions.

When used herein, these terms have the following meanings.

1. The term "mordant" means a compound which, when present in a composition, interacts with a dye to prevent diffusion through the composition.

2. The term "mordanting monomer" means a compound which, when copolymerized into a composition, will cause that copolymer to interact with a dye to prevent diffusion through the composition.

3. The term "SIPN" means a semi-interpenetrating network.

4. The term "semi-interpenetrating network" means an entanglement of a homocrosslinked polymer with a linear uncrosslinked polymer.

5. The term "crosslinkable" means capable of forming covalent or strong ionic bonds with itself or with a separate agent added for this purpose.

6. The terms "hydrophilic" and "hydrophilic surface" are used to describe a material that is generally receptive to water, either in the sense that its surface is wettable by water or in the sense that the bulk of the material is able to absorb significant quantities of water. Materials that exhibit surface wettability by water have hydrophilic surfaces.

7. The term "hydrophilic liquid-absorbing materials" means materials that are capable of absorbing significant quantities of water, aqueous solutions, including those materials that are water-soluble. Monomeric units will be referred to as hydrophilic units if they have a water-sorption capacity of at least one mole of water per mole of monomeric unit.

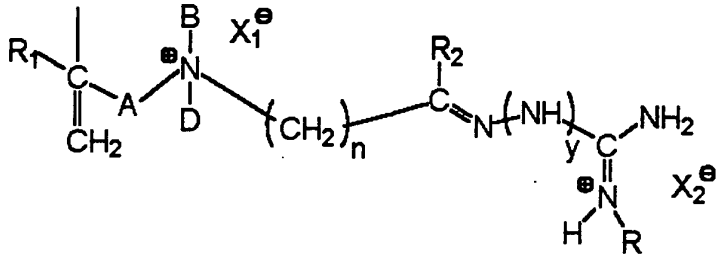
8. The terms "hydrophobic" and "hydrophobic surface" refer to materials which have surfaces not readily wettable by water. Monomeric units will be referred to as hydrophobic if they form water-insoluble polymers capable of absorbing only small amounts of water when polymerized by themselves.

All parts, percents, and ratios herein are by weight unless otherwise noted.

Detailed Description of the Invention

The imaging copolymer of the ink receptive layer of the present invention is formed from monomers including at least one mordanting monomer having a guanidinyl functionality.

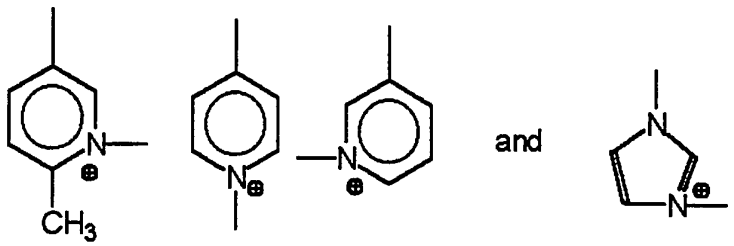
Useful mordanting monomers having have the following general structure:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 5 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CH_2O)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5, preferably from 1 to 3;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms, preferably from 1 to 3;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 5 carbon atoms;

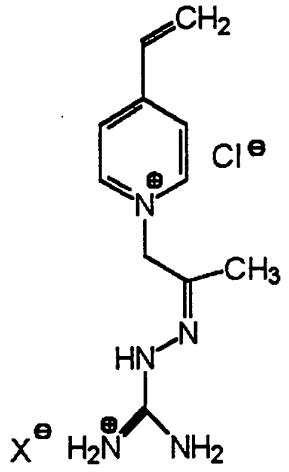
R is selected from the group consisting of hydrogen,

phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 5 carbon atoms, preferably from 1 to 3 carbon atoms;

y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions.

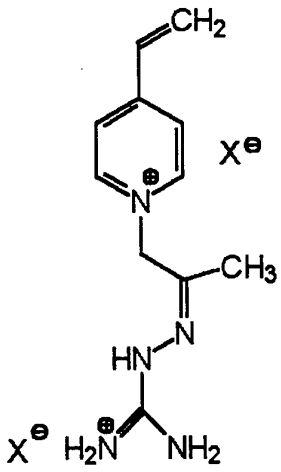
Preferred classes of mordanting monomers include the following:

Class A, which has a structure as follows:



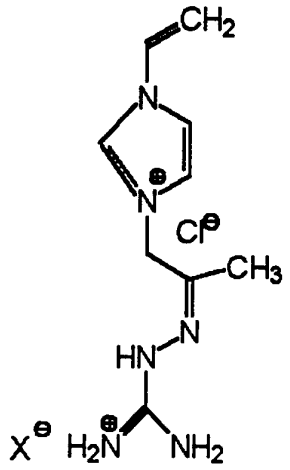
wherein X represents CH_3SO_3, Br, NO_3, Cl, CF_3COO, p-$MePhSO_3$, ClO_4, F, CF_3SO_3, BF_4, $C_4F_9SO_3$, FSO_3, PF_6, $ClSO_3$, or SbF_6; and n represents an integer of 2 or greater;

Class B, which has the structure:



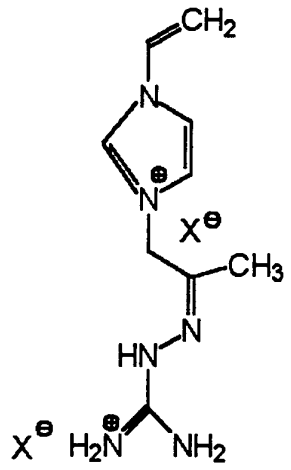
wherein X represents CH_3SO_3, p-$MePhSO_3$, CF_3SO_3, BF_4, PF_6, or SbF_6; and n represents an integer of 2 or greater.

Class C, which has the structure:



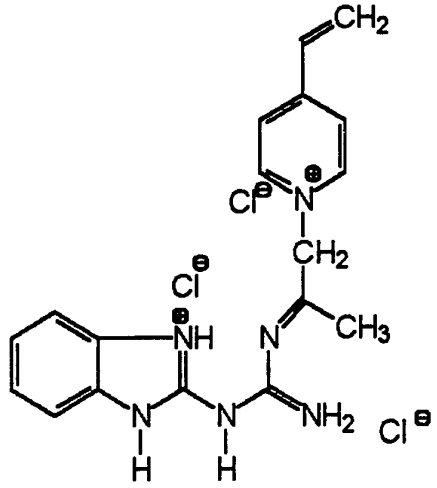
wherein X represents CH_3SO_3, Br, NO_3, Cl, CF_3COO, p-$MePhSO_3$, ClO_4, F, CF_3SO_3, BF_4, $C_4F_9SO_3$, FSO_3, PF_6, $ClSO_3$, or SbF_6; and n represents an integer of 2 or greater;

Class D, which has the structure:



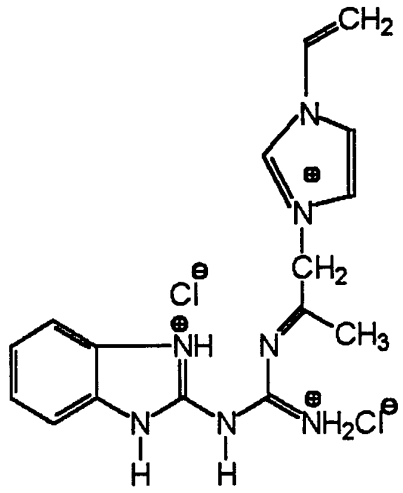
wherein X represents CH_3SO_3, p-$MePhSO_3$, CF_3SO_3, BF_4, PF_6, or SbF_6; and n represents an integer of 2 or greater;

Class E, which has the structure:



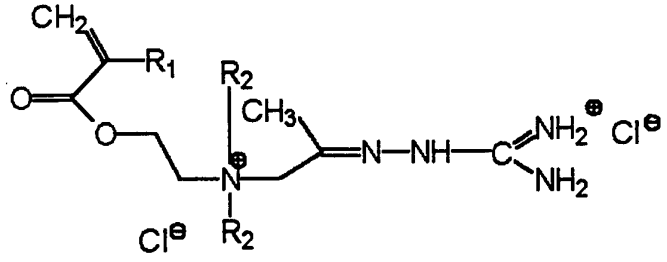
wherein n represents an integer of 2 or greater;

Class F which has the following structure:



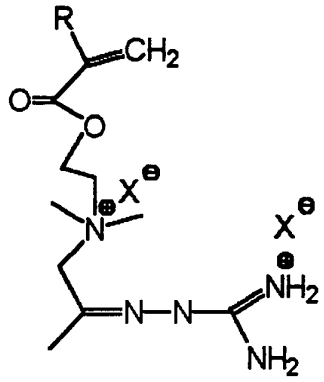
wherein n represents an integer of 2 or greater;

Class G which has the structure:



wherein R_1 represents H or CH_3; R_2 represents a C_1-C_4 alkyl group, and n represents an integer of 2 or greater.

Class H which has the structure:



wherein X is selected from the group consisting of Cl^-, and $CF_3SO_3^-$.

Preferred imaging copolymers are formed from monomers comprising at least one hydrophilic and liquid absorptive copolymerizable monomer. The monomers copolymerized to form preferred imaging copolymers comprise:

a) at least one nitrogen-containing hydrophilic, and water absorptive monomer selected from the group consisting of vinyl lactams such as N-vinyl-2-pyrrolidone; acrylamide, methacrylamide and their N-monoalkyl and N,N-dialkyl derivatives thereof; alkyltertiary-aminoalkylacryates and methacrylates; vinylpyridines such as 2-vinyl and 4-vinyl pyridines; preferably N-vinyl-2-pyrrolidone; acrylamide, methacrylamide and their N-monoalkyl and N,N-dialkyl derivatives thereof;

b) at least one hydrophilic monomer selected from the group consisting of hydroxyalkyl acrylate and methacrylate, the alkyl group having from about 1 to 5 carbon atoms, preferably from 1 to 2 carbon atoms, and more preferably hydroxyethyl acrylate and methacrylate; alkoxyalkyl acrylate and methacrylate, the alkyl group preferably ranging from 1 to 5 carbon atoms, preferably from 1 to 2 carbon atoms; and

c) at least one mordanting monomer having a formula described in classes A through H.

The imaging copolymer can be prepared by mixing the above monomers in various ratios. The nitrogen containing monomer is present from about 50 parts by weight to 95 parts by weight of the imaging copolymer, preferably from about 65 parts by weight to about 85 parts by weight. When less than about 50 parts by weight is used, the liquid absorbing properties of the imaging copolymer become too low for use in ink-receptive layers. When more than about 95 parts by weight are used, the integrity of the ink absorbing layer suffers as large amounts of liquid are absorbed.

The mordanting monomers are present in the imaging copolymer at from about 5 parts by weight to 40 parts by weight of the imaging copolymer, preferably from about 10 parts by weight to about 25 parts by weight. The lower amount is necessary for controlling bleed when imaged, especially with an aqueous based ink. At about 40 parts by weight, the mordanting effect seems to peak, and further improvement is not achieved without other modifications to the imaging copolymer or the absorption layer.

The non-nitrogen containing hydrophilic monomer is chosen to be less hydrophilic than the nitrogen contain ones. The presence of this monomer helps in reducing curl in the finished product without a separate anticurling compound or layer.

Useful amounts of hydrophilic monomers are in the range of from 0 parts to 10 parts by weight of the imaging copolymer, preferably from about 5 parts by weight to about 10 parts by weight.

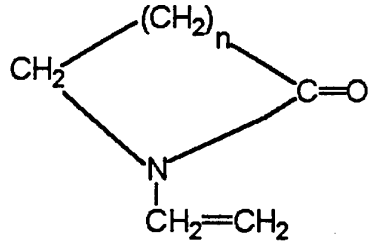
The imaging copolymer is preferably prepared by free radical solution polymerization of the monomers using free radical initiators, usually in the amount of about 0.01-2.0 parts by weight of the imaging copolymer. The

polymerization can be carried out in an aqueous or solvent medium, preferably aqueous medium.

The imaging copolymer can be crosslinked with a suitable crosslinking agent. The crosslinking, if desired, is generally done after the imaging copolymer has been coated onto a substrate.

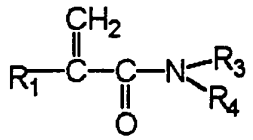
To form a liquid absorbing layer, the imaging copolymer can be mixed with a liquid absorbent polymeric component capable of absorbing water, and preferably a polymer that is water-soluble. Useful liquid absorbent polymers include those formed from the following monomers:

(1) vinyl lactams having the repeating structure:



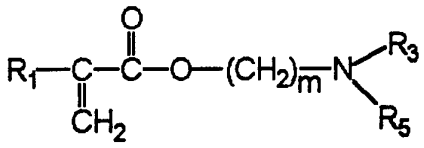
where n represents the integer 2 or 3;

(2) acrylamide or methacrylamide having the structure:



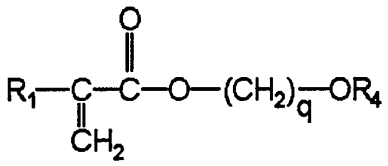
where R_1 is as defined previously, R_3 represents H or an alkyl group having up to ten carbon atoms, preferably from one to four carbon atoms, and R_4 represents H or an alkyl group, having up to ten carbon atoms, preferably from one to four carbon atoms, or an hydroxyalkyl group, or an alkoxy alkyl group having the structure of $-(CH_2)_p-OR_3$, where p represents an integer from 1 to 3, inclusive;

(3) tertiary amino alkylacrylates or tertiary amino alkylmethacrylates having the structure:



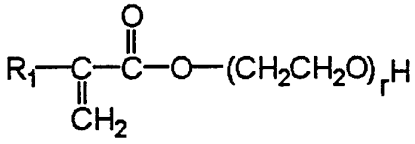
where m represents the integer 1 or 2 and R_1 and R_3 are as defined previously, and R_5 represents an alkyl group having up to ten carbon atoms, preferably from one to four carbon atoms;

(4) hydroxy alkylacrylates, alkoxy alkylacrylates, hydroxy alkyl methacrylates, or alkoxy alkyl methacrylates having the structure:



where R_1 and R_4 are as defined previously, q represents an integer from 1 to 4, inclusive, preferably 2 to 3; and

(5) alkoxy acrylates or alkoxy methacrylates having the structure:



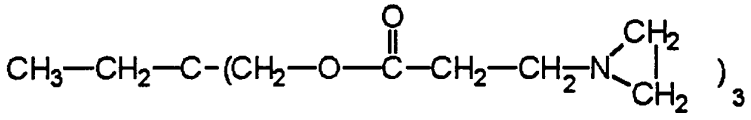
where r represents an integer from 5 to 25, inclusive, and R_1 is defined previously.

Some of the previously mentioned structures of both the hydrophobic and hydrophilic monomeric units contain pendant ester groups that can readily be rendered crosslinkable by hydrolysis. For the others, monomeric units containing acidic groups are incorporated into the polymeric structure to render them crosslinkable. Polymerization of these monomers can be carried out by

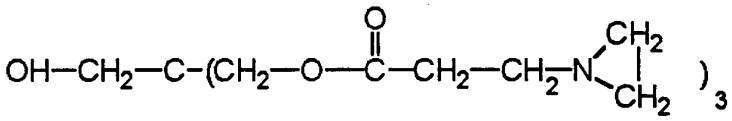
typical free radical solution, emulsion, or suspension polymerization.

When crosslinking of the imaging copolymer is desired, the image receptive layer typically comprises from about 0.5 to 6.0 parts by weight of a crosslinking agent per 100 parts by weight of the layer, preferably from about 1.0 to 4.5 parts by weight. The imaging copolymer can comprise from about 24.5 to about 93 parts by weight, preferably from about 29 to 55.5 parts by weight of the total layer. The liquid absorbent component can comprise from about 1 to about 75 parts, preferably from about 40 to about 70 parts by weight of the total layer.

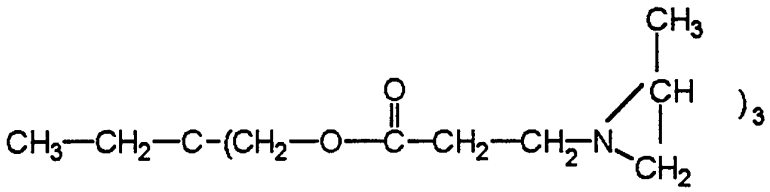
The imaging copolymer is preferably crosslinked with polyfunctional aziridines possessing at least two crosslinking sites per molecule, such as trimethylol propane-tris-(β-(N-aziridinyl)propionate)



pentaerythritol-tris-(β-(N-aziridinyl)propionate)



trimethylolpropane-tris-(β-(N-methylaziridinyl propionate)



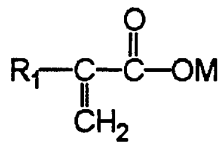
and so on. Crosslinking can also be brought about by means of metal ions, such as provided by multivalent metal ion salts, provided the composition containing the crosslinkable polymer is made from 80 to 99 parts by

weight of monomer and from 1 to 20 parts by weight of a chelating compound.

The metal ions can be selected from ions of the following metals: cobalt, calcium, magnesium, chromium, aluminum, tin, zirconium, zinc, nickel, and so on, with the preferred compounds being selected from aluminum acetate, aluminum ammonium sulfate dodecahydrate, alum, aluminum chloride, chromium (III) acetate, chromium (III) chloride hexahydrate, cobalt acetate, cobalt (II) chloride hexahydrate, cobalt (II) acetate tetrahydrate, cobalt sulfate hydrate, copper sulfate pentahydrate, copper acetate hydrate, copper chloride dihydrate, ferric chloride hexahydrate, ferric ammonium sulfate dodecahydrate, ferrous chloride, tetrahydrate, magnesium acetate tetrahydrate, magnesium chloride hexahydrate, magnesium nitrate hexahydrate, manganese acetate tetrahydrate, manganese chloride tetrahydrate, nickel chloride hexahydrate, nickel nitrate hexahydrate, stannous chloride dihydrate, stannic chloride, tin (II) acetate, tin (IV) acetate, strontium chloride hexahydrate, strontium nitrate, zinc acetate dihydrate, zinc chloride, zinc nitrate, zirconium (IV) chloride, zirconium acetate, zirconium oxychloride, zirconium hydroxychloride, ammonium zirconium carbonate, and so on.

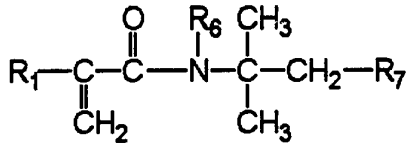
The preferred chelating compounds can be selected from:

(1) alkaline metal salts of acrylic or methacrylic acid having the structure:



where R_1 is described previously and M represents Li, Na, K, Rb, Cs, or NH_4, preferably NH_4, Na, or K;

(2) N-substituted acrylamido or methacrylamido monomers containing ionic groups having the structure:



where R_1 is described previously, R_6 represents H or an alkyl group having up to four carbon atoms, preferably H, R_7 represents COOM or $-SO_3M$ where M is described previously;

(3) alkali metal salt of p-styrene sulfonic acid;

(4) sodium salt of 2-sulfo ethyl acrylate and sodium salt of 2-sulfo ethyl methacrylate;

(5) 2-vinyl pyridine and 4-vinyl pyridine;

(6) vinyl imidazole;

(7) N-(3-aminopropyl) methacrylamide hydrochloride; and

(8) 2-acetoacetoxy ethyl acrylate and 2-acetoacetoxy ethyl methacrylate.

Polymerization of these monomers can be carried out by conventional free radical polymerization techniques as mentioned previously.

Alternately, the liquid-absorbent component can be selected from commercially available water-soluble or water-swellable polymers such as polyvinyl alcohol, polyvinyl alcohol/poly(vinyl acetate) copolymer, poly(vinyl formal) or poly(vinyl butyral), gelatin, carboxy methylcellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl starch, poly(ethyl oxazoline), poly(ethylene oxide), poly(ethylene glycol), poly(propylene oxide), and so on. The preferred polymers are poly(vinyl lactams), especially poly(vinyl pyrrolidone), and poly(vinyl alcohol).

SIPNs to be used for forming ink-receptive layers of the present invention typically comprise from about 0.5 to 6.0 percent crosslinking agent, preferably from about 1.0

to 4.5 percent, when crosslinking agents are needed. The crosslinkable polymer can comprise from about 25 to about 99 percent, preferably from about 30 to about 60 percent of the total SIPNs. The liquid-absorbent component can comprise from about 1 to about 75 percent, preferably from about 40 to about 70 percent of the total SIPNs.

The ink-receptive layer can also include particulate material for the purpose of improving handling and flexibility. Preferred particulate materials include polymeric beads, e.g., poly(methylmethacrylate), poly(stearyl methacrylate)hexanedioldiacrylate copolymers, poly(tetrafluoroethylene), polyethylene; starch and silica. Poly(methylmethacrylate) beads are most preferred. Levels of particulate are limited by the requirement that the final coating be transparent with a haze level of 15% or less, as measured according to ASTM D1003-61 (Reapproved 1979). The preferred mean particle diameter for particulate material is from about 5 to about 40 micrometers, with at least 25% of the particles having a diameter of 15 micrometers or more. Most preferably, at least about 50% of the particulate material has a diameter of from about 20 micrometers to about 40 micrometers.

The ink-receptive formulation can be prepared by dissolving the components in a common solvent. Well-known methods for selecting a common solvent make use of Hansen parameters, as described in U.S. 4,935,307, incorporated herein by reference.

The ink-receptive layer can be applied to the film backing by any conventional coating technique, e.g., deposition from a solution or dispersion of the resins in a solvent or aqueous medium, or blend thereof, by means of such processes as Meyer bar coating, knife coating, reverse roll coating, rotogravure coating, and the like.

Drying of the ink-receptive layer can be effected by conventional drying techniques, e.g., by heating in a hot air oven at a temperature appropriate for the specific film backing chosen. For example, a drying temperature of

about 120°C is suitable for a polyester film backing.

In an alternative embodiment of the present invention, an ink-permeable protective layer is applied atop the ink-receptive layer to form a composite medium for sorbing liquids. In this embodiment, either layer of the composite may contain the mordanting monomer, or mordanting monomers may be contained in both layers.

If the mordanting monomer is present in the surface layer, it is also copolymerized with other monomers suitable for use in the liquid-permeable layer. However, a polymeric mordant having a guanidine group may also separately be blended into the ink-permeable layer, if desired. Preferably, the mordanting monomer is present in the liquid-sorbent underlayer.

The ink-receptive layer will typically have greater liquid sorptivity than that of the surface layer whereby the composite medium has a sorption time less than the sorption time of a thickness of the surface layer equal to the thickness of the composite medium.

The liquid sorptivity can be tested by a "sorption time" or "dry time" test or other analogous tests such as those disclosed in U.S. Patent 4,379,804, incorporated herein by reference.

Preferred materials for the ink-permeable layer include polyvinyl alcohol, polyvinyl pyrrolidone, cellulose acetate/butyrate, gelatin, polyvinyl acetate and mixtures thereof. Polyvinyl alcohol is the most preferred material.

Additives can also be incorporated into the ink-permeable layer to improve processing, including thickeners such as xanthan gum, added to improve coatability, particulates to improve feedability, and sols such as alumina or silica sols to improve image quality.

Other suitable materials for the ink-permeable layer are disclosed in U.S. Patent Nos. 4,225,652, 4,301,195, and 4,379,804, all of which are incorporated herein by reference.

The composition for the liquid-permeable layer is preferably prepared by dispersing finely divided polyvinyl alcohol in cold water, agitating the dispersion vigorously, and then gradually heating the dispersion by an external source or by a direct injection of steam. After cooling the dispersion to room temperature, particulate material can be mixed into the dispersion using conventional propeller type power-driven apparatus.

Methods for applying the ink-permeable layer are conventional coating methods such as those described, supra.

Film backings may be formed from any polymer capable of forming a self-supporting sheet, e.g., films of cellulose esters such as cellulose triacetate or diacetate, polystyrene, polyamides, vinyl chloride polymers and copolymers, polyolefin and polyallomer polymers and copolymers, polysulphones, polycarbonates and polyesters.

While transparent backings are preferred, especially where applications such as image projection are desired, the scope of this invention includes the use of opaque backings such as vinyl, nontransparent polyolefins and the like. These opaque backings are especially useful in larger format applications such as those for advertising on signs, buildings, panels for motor vehicles and the like, but may also be useful in office sized format for presentations where projection is not required, indoor advertisements, placards, brochures and the like.

Suitable polyester films may be produced from polyesters obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters in which the alkyl group contains up to about 6 carbon atoms, e.g., terephthalic acid, isophthalic, phthalic, 2,5-,2, 6-, and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, with one or more glycols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and the like.

Preferred film backings are cellulose triacetate or cellulose diacetate, polyesters, especially poly(ethylene terephthalate), and polystyrene films. Poly(ethylene terephthalate) is most preferred. It is preferred that film backings have a caliper ranging from about 50 micrometers to about 125 micrometers. Film backings having a caliper of less than about 50 micrometers are difficult to handle using conventional methods for graphic materials. Film backings having calipers over 125 micrometers are very stiff, and present feeding difficulties in certain commercially available ink jet printers and pen plotters.

When polyester or polystyrene films supports are used, they are preferably biaxially oriented, and may also be heat set for dimensional stability during fusion of the image to the support. These films may be produced by any conventional method in which the film is biaxially stretched to impart molecular orientation and is dimensionally stabilized by heat setting.

To promote adhesion of the ink-receptive layer or layers to the film backing, it may be desirable to treat the surface of the film backing with one or more primers, in single or multiple layers. Useful primers include those known to have a swelling effect on the film backing polymer. Examples include halogenated phenols dissolved in organic solvents. Alternatively, the surface of the film backing may be modified by treatment such as corona treatment or plasma treatment.

The primer layer, when used, should be relatively thin, preferably less than 2 micrometers, most preferably less than 1 micrometer, and may be coated by conventional coating methods.

Where desired, the opposing surface of the substrate to the imaging surface may be coated with an adhesive in order to facilitate attachment to a bulletin board, billboard or the like or use of an opaque sheet to form an ink-receptor composite. The adhesive may cover only a

portion, or the entire opposing major surface may be coated therewith. Useful adhesives are conventional adhesives including such nonlimiting examples as hot melt adhesives, rubber adhesives, block copolymer adhesives, pressure-sensitive adhesives, acrylate adhesives, repositionable microsphere adhesives and the like.

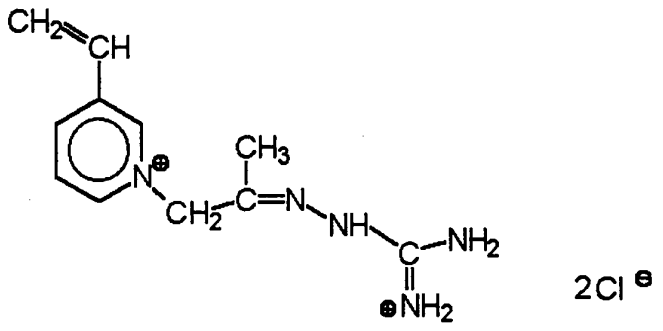
Where an adhesive is coated onto ink-receptive sheets of the invention, an additional sheet, known as a "low adhesion backsize" may also be present. The purpose of such a sheet, is to cover and protect the adhesive, until such time as it is desirable to expose the adhesive for attachment. The sheet may be comprised of any material, such as a film or paper, which has a low adhesion to the particular adhesive chosen, or it may be coated with a release material such as a silicone.

Transparent ink-receptive sheets of the invention or "transparencies" of the invention are particularly useful in the production of imaged transparencies for viewing in a transmission mode, e.g., in association with an overhead projector.

The following examples are for illustrative purposes, and do not limit the scope of the invention, which is that defined by the claims.

Glossary of Mordanting Monomers

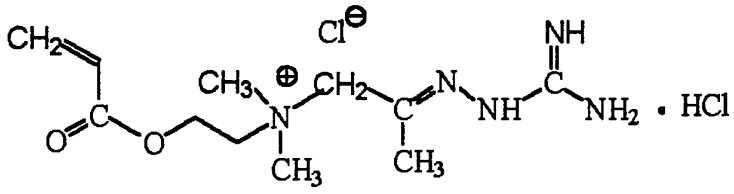
P144



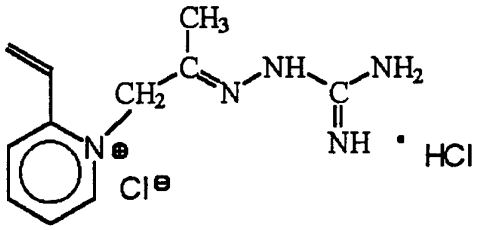
P134-Class A mordanting monomer wherein the anion, X^-, is CF_3SO_3. When another anion is used, the designation will be followed by the identity of the anion.

I224-Class C mordanting monomer wherein X^-, is $CF_3SO_3^-$. When another anion is used, the designation will be followed by the anion.

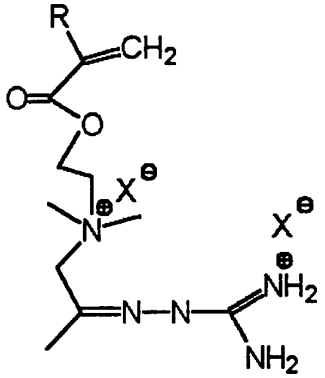
MA1-CMA1-Cl^-



P124

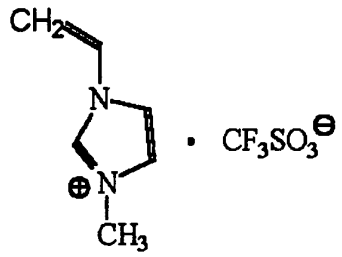


F-71 Class H mordanting monomer wherein X^- is Cl^-. When another anion is used, the designation will be followed by the anion.

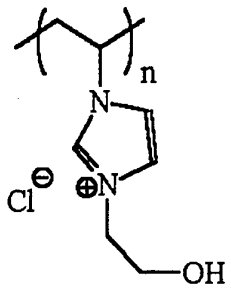


The following are comparative mordants.

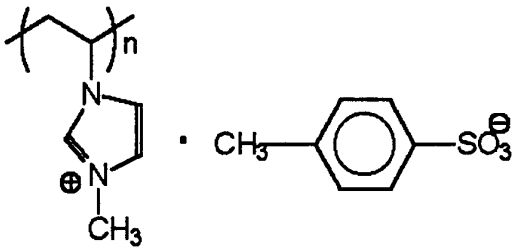
MI-CF_3SO_3



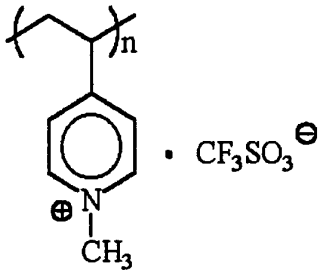
HEI-Cl^-



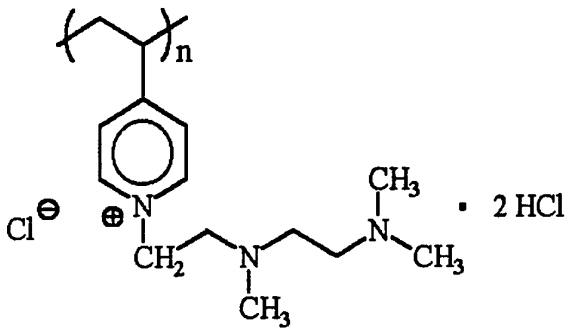
MI-PTSA



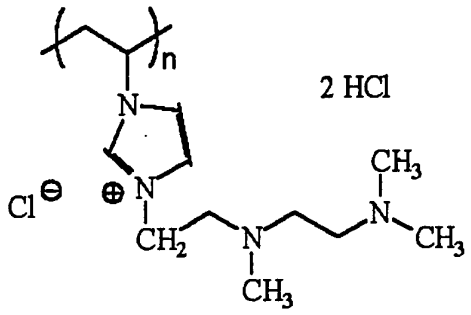
MP-$CF_3SO_3^-$



P132



I222



Examples

Synthesis of mordants

1. Synthesis of Dimethylaminomethacrylate-chloroacetone aminoguanidine hydrazone adduct (DMAEMA-G)

100 parts of Dimethylaminoethylmethacrylate (DMAEMA) were introduced to a reaction vessel fitted with a mechanical stirrer, a condenser, and a dropping funnel. 117.1 parts of Chloroacetone hydrazone aminoguanidine hydrazone (CAHAGH) in 285 parts of methanol were added to the vessel from the dropping funnel while cooling the vessel in a cold water bath. An exotherm of 50°C was observed. After completing the addition of CAHAGH, the reaction mixture was stirred at room temperature for about 2 hours, followed by removal of the organic solvent by rotary evaporation under vacuum at 40°C. A white solid of DMAEMA-G was obtained and this was confirmed to be DMAEMA-G by ^{1}H NMR spectroscopy.

2. Synthesis of 1-vinylimidazole-chloroacetone aminoguanidine hydrazone adduct (VIMD-G)

10 parts of 1-vinylimidazole and 20 parts of ethanol were introduced to a reaction vessel fitted with a magnetic stirrer, a condenser and a thermometer. 59.24 parts of a 33% ethanol solution of CAHAGH were then added. The mixture was stirred at room temperature. After 5 minutes, an exotherm of about 40°C was observed. After 15 minutes, the reaction mixture started to cool and a white solid precipitated. After the reaction mixture was stirred for another 30 minutes, the temperature of the contents dropped to room temperature. 20 parts of D.I. water were then added. A clear solution was formed at this point. After removal of the solvent by rotatory evaporation at 40°C under vacuum, a white solid was formed. This was confirmed to be VIMD-G by ^{1}H NMR spectroscopy.

3. Synthesis of vinyldimethyl azlactone-aminoguanidine hydrochloride (VDM-G) adduct.

25.3 parts of vinyldimethylazlactone (VDM) were charged into a reaction vessel. To the vessel was then added a suspension of 20 parts of aminoguanidine hydrochloride (AGH) in 30 parts of water. Within 5 minutes of the addition, an exotherm was observed and a white powder started to precipitate. The mixture was stirred for about an hour and the solvent was removed by rotary evaporation under vacuum at 40°C to produce a white powder. This was confirmed to be VDM-G by ^{1}H NMR spectroscopy.

Synthesis of Imaging Copolymer A

61.0 g of N-vinyl-2-pyrrolidone, 15 g of 2-hydroxyethylmethacrylate 20 g of DMAEMA-G, 4 g of acrylic acid (AA) neutralized to pH 7 with NH_4OH, 0.6 g of VAZO® 52 from DuPont, 125.6g of D.I. water and 107.8 g of ethanol were charged to a brown quart bottle. The solution was purged with N_2 gas for about 10 minutes and

then the bottle and its contents were immersed in a constant temperature bath kept at 50° C. After reacting for about 24 hours, a 96.5 % conversion was obtained at 28% solid. This was diluted with a 4:1 mixture of D.I.water/ethanol.

Synthesis of Imaging Copolymer B

50 g of n-vinyl-2-pyrrolidone, 15 g of 2-hydroxyethylmethacrylate, 15 g of methoxyethylacrylate, 16 g of monomer VIMD-G, 4g of AA neutralized with NH_4OH, 0.4 g of VAZO 52, 220g of D.I. water and 80 g of ethanol were charged into a one quart brown bottle. The solution was purged with N_2 gas for about 10 minutes and then the bottle and its contents were immersed in a constant temperature bath kept at 50° C. After reacting for about 18 hours, a 90.2% conversion was obtained at 22.6% solid. This was diluted with a 4:1 mixture of D.I.water/ethanol.

Synthesis of Imaging Copolymer C

25 g of n-vinyl-2-pyrrolidone, 7.5 g of 2-hydroxyethylmethacrylate, 7.5 g of methoxyethylacrylate, 8 g of monomer VDM-G, 2g of AA neutralized with NH_4OH, 0.2 g of VAZO 52, 110g of D.I. water and 40 g of ethanol were charged into a one quart brown bottle. The solution was purged with N_2 gas for about 10 minutes and then the bottle and its contents were immersed in a constant temperature bath kept at 50°C. After reacting for about 16 hours, a 98.9% conversion was obtained at 24.7% solid. This was diluted with a 4:1 mixture of D.I.water/ethanol.

Example 1

10.25 g of imaging copolymer A was blended with 8 g of 10% aqueous solution of Airvol 523 from AirProducts Chemical Co., 2 g of 10% aqueous solution of KPO_3, 0.42 g of a 10% aqueous suspension of 30 μ PMMA beads and 0.92 g of a 10% aqueous solution of XAMA-7 to give a coating

solution. The solution was knife coated onto a 100 μ thick polyester terephthalate (PET) film that had been primed with polyvinylidiene chloride (PVDC) at a wet coating thickness of about 150 μm. This was dried in an oven at about 215°C for about 3 minutes. The sample was then imaged on HP Deskjet 500C.

After keeping the imaged film at ambient condition for 10 minutes, it was stored in transparency protector and aged at 35°C and 80% RH for 76 hours. The sample was then tested according to the test method described above and showed 22.2% bleed.

Example 2

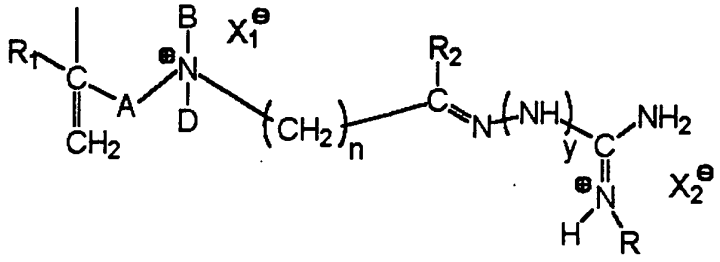
This was made in the same manner as Example 1, except that imaging copolymer B was used and no crosslinker was present in the coating solution. The imaged sheet was aged at ambient condition for 5 minutes before being introduced into a transparency protector. The Bleed test was done after 76 hours and showed 61.1% bleed.

Example 3

A coating solution of 49.2 parts of a 10% aqueous solution of imaging copolymer C, 49.2 parts of a 10% aqueous solution of polyvinylalcohol and 1.6 parts of a 10% aqueous solution was coated and dried as in Example 1. The sample was then imaged on HP Deskjet 500C. After keeping the imaged film at ambient condition for 10 minutes, it was stored in transparency protector and aged at 35° C and 80% RH for 72 hours. The sample was then tested as in Example 1 and showed 55.6% bleed.

What is Claimed is:

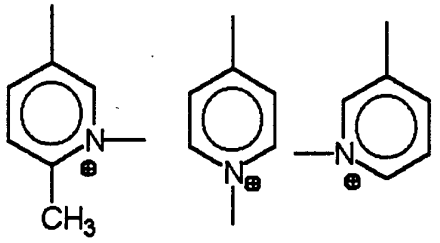
1. An ink-receptive sheet comprising a substrate bearing on at least one major surface thereof, an ink-receptive layer comprising an imaging copolymer formed from monomers comprising at least one mordanting monomer having a guanidinyl functionality of the following general formula:



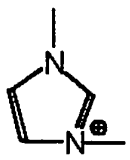
wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



and



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms;

R is selected from the group consisting of hydrogen,

phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and

X_1 and X_2 are anions.

2. An ink-receptive sheet according to claim 1 wherein said anion is selected from the group consisting of Cl^-, Cf_3COO^-, phenyl-$CH_3SO_3^-$, BF_4^-, $CH_3SO_3^-$, NO_2^-, Br^- and $CF_3SO_3^-$.

3. An ink-receptive sheet comprising a transparent substrate bearing on at least one major surface thereof, an ink-receptive layer comprising an imaging copolymer formed from monomers comprising:

a) at least one nitrogen-containing hydrophilic and water absorptive monomer selected from the group consisting of vinyl lactams, alkyltertiary-aminoalkylacryates, alkyltertiary aminomethacrylates, and vinylpyridines;

b) at least one hydrophilic monomer selected from the group consisting of hydroxyalkyl acrylate and methacrylate, alkoxyalkyl acrylate and methacrylate, each monomer containing an alkyl group having from 1 to 5 carbon atoms;

c) at least one mordanting monomer comprising a guanidinyl functionality according to claim 1.

4. An ink-receptive sheet according to claim 3 wherein said vinyl lactam is selected from the group consisting of N-vinyl-2-pyrrolidone, acrylamide, methacrylamide and the N-monoalkyl and N,N-dialkyl derivatives thereof, and said vinylpyridine is selected from the group consisting of 2-vinyl and 4-vinyl pyridines.

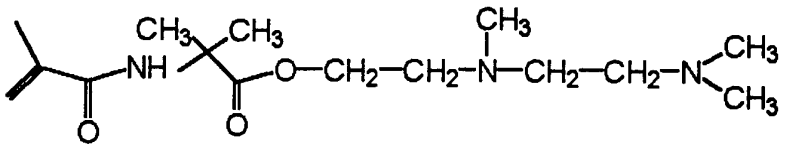
5. An ink-receptive sheet comprising as an ink-receptive layer, a crosslinked semi-interpenetrating network formed from:

a) at least one crosslinkable polymeric component formed from monomers comprising at least one mordanting monomer according to claim 1,

b) at least one liquid-absorbent polymeric component, and

c) optionally, a crosslinking agent.

6. An ink-receptive sheet according to claim 1 wherein said mordanting monomer has the following formula:



7. An ink-receptive sheet according to claim 1 wherein said substrate is selected from the group consisting of cellulose esters, polyamides, vinyl chloride polymers and copolymers, polyolefin and polyallomer polymers and copolymers, polysulphones, and polycarbonates.

8. An ink-receptive sheet according to claim 1 wherein said substrate is transparent.

9. An ink-receptive sheet comprising a transparent substrate bearing on at least one major surface thereof an ink-receptive layer comprising:

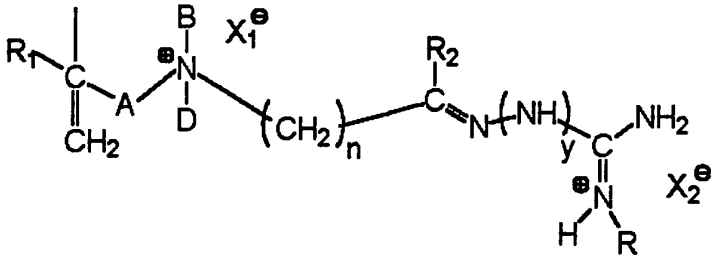
a) at least one crosslinkable component formed from monomers comprising:

1) at least one hydrophilic nitrogen-containing monomer,

2) at least one ethylenically α,β-

unsaturated monomer, and

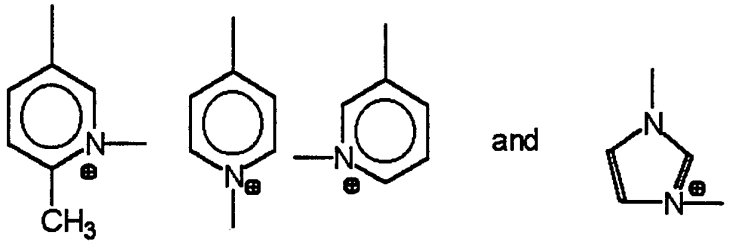
3) at least one mordanting monomer comprising a guanidinyl functionality having the following general structure:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 3 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions,

b) at least one liquid-absorbent polymeric component,

c) a polyfunctional aziridine crosslinking agent, and

e) a particulate material having a particle size distribution ranging from the about 5 μ to about 40 μm.

10. An ink-receptive sheet according to claim 9 wherein said hydrophilic nitrogen-containing monomer comprises from about 50 to about 95 parts by weight of said imaging polymer, said ethylenically α,β-unsaturated monomer comprises from about 5 to about 10 parts by weight, and said mordanting monomer comprises from about 5 to about 40 parts by weight, per 100 parts of said imaging copolymer.

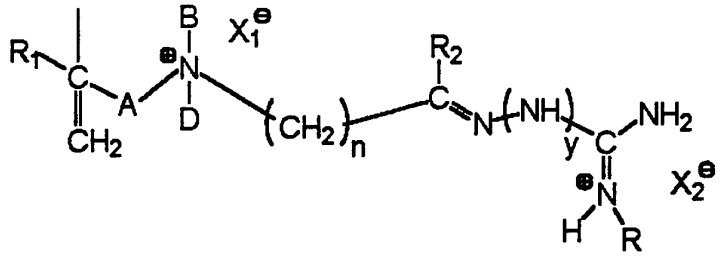
11. An ink-receptive sheet comprising a substrate bearing on at least one major surface a two-layer composite medium for sorbing liquids comprising:

a) a liquid-sorbent underlayer comprising an imaging copolymer, and overlying said underlayer,

b) a liquid-permeable surface layer,

the liquid sorbtivity of said underlayer being greater then the liquid sorptivity of said surface layer whereby the composite medium has a sorption time less than the sorption time of a thickness of said surface layer equal to the thickness of the composite medium,

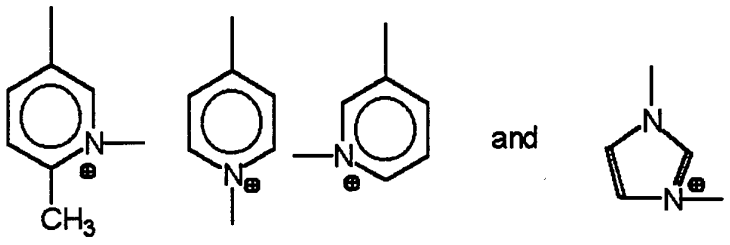
wherein at least one layer comprises a copolymer formed from monomers comprising at least one mordanting monomer having a guanidinyl functionality having the following general formula:



wherein A is selected from the group consisting of a COO-alkylene group having from about 1 to about 5 carbon atoms, a CONH-alkylene group having from about 1 to about 3 carbon atoms, $-COO-(CH_2CH_2O)n-CH_2-$, $-CONH-(CH_2CHO)n-CH_2-$, and $-(CH_2-CH_2-NH_2Cl)n-$, wherein n is from about 1 to about 5;

B and D are separately selected from the group consisting of alkyl group having from about 1 to about 5 carbon atoms;

or A, B, D and N are combined to form a heterocyclic compound selected from the group consisting of



R_1 and R_2 are independently selected from the group consisting of hydrogen, phenyl, and an alkyl group containing from about 1 to about 3 carbon atoms;

R is selected from the group consisting of hydrogen, phenyl, benzimidazolyl, and an alkyl group containing from about 1 to about 3 carbon atoms,

y is selected from the group consisting of 0 and 1, and X_1 and X_2 are anions.

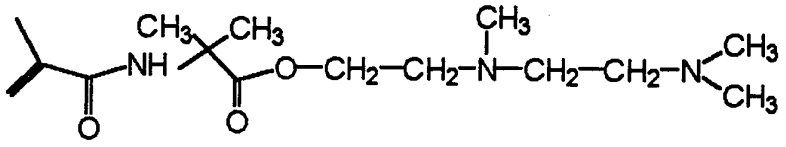
12. An ink-receptive sheet according to claim 11 wherein liquid-sorbent underlayer comprises an imaging

copolymer formed from monomers comprising at least one monomer having a guanidinyl functionality.

13. An ink-receptive sheet according to claim 11 wherein liquid-permeable surface layer comprises a copolymer formed from monomers comprising at least one monomer having a guanidinyl functionality.

14. An ink-receptive sheet according to claim 11 wherein each of said layers comprises a copolymer formed from monomers comprising at least one monomer having a guanidinyl functionality.

15. An ink-receptive sheet according to claim 11 wherein at least one of said layers comprises a mordanting monomer having the following formula:



16. An ink receptive sheet according to claim 1 further comprising a sol selected from the group consisting of alumina sols and silica sols.

17. An ink receptive sheet according to claim 11 wherein at least one layer further comprises a sol selected from the group consisting of alumina sols and silica sols.

18. An ink-receptive sheet according to claim 1 wherein said ink-receptive layer further comprises a particulate.

19. An ink-receptive sheet according to claim 18 comprising a first particulate and a second particulate wherein said first particulate is a polymeric particulate

having a average size of from about 5 μm to about 40 μm, and said second particulate has an average size of from about 0.25 μm to about 1 μm.

20. An ink-receptive sheet according to claim 20 wherein said substrate is transparent.

INTERNATIONAL SEARCH REPORT

Inte: ɔnal Application No
PCT/US 94/02677

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B41M5/00

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 5 B41M G03C

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.
A	EP,A,0 211 273 (3M) 25 February 1987 cited in the application see claims 1-12	1-20

☐ 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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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 1994	07.07.94

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	Fouquier, J-P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte: ɔnal Application No
PCT/US 94/02677

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0211273	25-02-87	AU-B-	586872	27-07-89
		CA-A-	1268986	15-05-90
		JP-A-	62070830	01-04-87
		US-A-	4695531	22-09-87