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(54) **Ink jet image-forming process**

(57) A process for forming images comprising ink jet printing on a recording sheet containing a dye fade-preventing agent using at least one aqueous ink comprising a water-soluble acid or direct dye. Suitable agents are phenol derivatives wherein at least one of the ortho-positions with respect to the hydroxy group is substituted by a tertiary alkyl group; bisphenol derivatives; phenol derivatives of phosphoric acid esters; and phenol compounds wherein the *p*-position with respect to the hydroxy group is substituted by an oxygen atom forming part of a 5- or 6-membered ring which is condensed together with the phenol nucleus. The agent is coated with a pigment or onto a pigment-containing layer on the sheet, preferably together with an hydroquinone antioxidant and/or ultraviolet absorbent. Multi-colour images using yellow, magenta, cyan and black inks are provided with excellent fading resistance.

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SPECIFICATION

Ink jet recording image-forming process

This invention relates to an ink jet printing process. More particularly, the invention relates to an ink jet printing process suitable for the formation of multicolor recording images. More particularly, the invention relates to an ink jet printing process which is excellent in color reproducibility and suitable for forming multicolor recording images having excellent light resistance.

Since ink jet printing process makes less noise, can employ high speed recording, and can use plain paper for recording, this printing process has been employed for terminal printers, etc., and recently has been increasingly ued for various purposes. Furthermore, a system of forming multicolor recorded images using multiple ink nozzles has been widely used for color plotters and color facsimiles. However, in the case of practicing multicolor recording, various problems occur which have not occurred in the case of monochromatic recording.

That is, unlike monochromatic recording, multicolor recording is usually used for forming reproduced images, such as photographs, pictures, posters, illustrations, color images, etc., and involves the followng problems:

(1) Reproduced images faithfully reproducing forms, colors and sharpness of photographs, pictures, posters, illustrations, color images, etc., must be formed.

(2) Reproduced image portions faithfully reproducing photographs, pictures, posters, illustrations, color images, etc., and non-images portions may become stained when they are exposed to ultraviolet rays for a long period of time.

(3) Reproduction images of photographs, pictures, posters, illustrations, color images, etc., must be stably formed at a high speed.

(4) During ink jet printing, ink flows may be scattered so as to stain the non-imaged portions.

(5) When the printed portions are rubbed after printing, the imaged portions may be disturbed and the non-imaged portions stained.

For solving these problems, various attempts have been proposed. For example Japanese Patent Application (OPI) No. 89811/79 (the term "OPI" as used herein refers to a "published unexamined Japanese patent application") discloses an ink jet printing process using yellow, magenta, and cyan inks, the reflection density curves of which shown on a medium are restricted for performing color reproduction necessary for forming reproduction images faithfully reproducing original images. Also, Japanese Patent Application (OPI) No. 89534/74 discloses a printing process using yellow, magenta and cyan inks for forming stable reproduction images faithful to the original images at a high speed.

Japanese Patent Application (OPI) No. 530121/77 discloses ink jet recording papers for obtaining images having good density, resolving power and color reproducibility. Particularly, a coating material is coated on a slightly sized base paper and the coating material permeates to the inside of the paper to reduce spreading of color components in the inks in the planar directions of the paper, reduces the permeation of color components in the inks to the inside of the paper, and thus keeps the color components at the surface of the paper. Furthermore, for similar purposes, Japanese Patent Application (OPI) No. 49113/78 discloses ink jet recording papers prepared by impregnating papers containing a fine powder of urea-foramalin resin with a water-soluble polymer, and Japanese Patent Application (OPI) No. 74340/77 discloses ink jet recording papers having definite gas permeability and ink absorbing time. Also, for preventing reproduced images obtained by ink jet printing for a long period of time without fading, Japanese Patent Application (OPI) Nos. 68303/79 and 85804/79 disclose inks containing water-soluble ultraviolet absorbents.

However, the multicolor recording images formed by using these known techniques cannot sufficiently meet all desired characteristics of color reproduction and light resistance, and thus these techniques are not completely satisfactory as ink jet printing processes.

An object of this invention is to provide an ink jet printing process suitable for forming multicolor recording images having high color density, excellent resolution and good color reproducibility.

Other object of this invention is to provide an ink jet printing process suitable for forming multicolor recording images which can be preserved for a long period of time and are excellent in light resistance.

Still other object of this invention is to provide an ink jet printing process using yellow, magenta, cyan, and black inks having excellent light resistance and color reproducibility, and a recording sheet having a coating layer containing a dye image fading preventing agent.

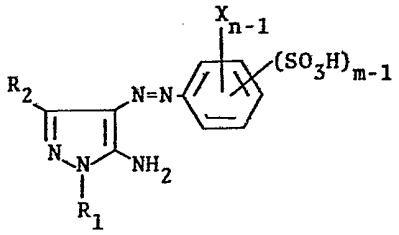
As a result of extensive investigations, it has been discovered that in an image forming process by ink jet printing, images having very high light resistance can be formed by ink jet printing onto a recording sheet containing a dye image fading preventing agent at least one aqueous ink comprising a water-soluble acid dye or water-soluble direct dyes.

Multicolor recorded images having high color density, excellent resolution, excellent color reproducibility, and excellent light fading resistance can be formed by ink jet printing onto a recording sheet having a pigment-coated layer containing a dye image facing preventing agent, using aqueous ink(s) as described above.

According to this invention, inks suitable for forming multicolor recording images include yellow, magenta, cyan and black inks, desirably having high light resistance, desirable spectral absorption region and minimal side absorption; as dyes used for such inks, water-soluble acid dyes or water-soluble direct dyes are useful.

Preferred dyes are those shown by following general formulæ:

Preferred yellow dyes used in this invention are shown by formula (I):



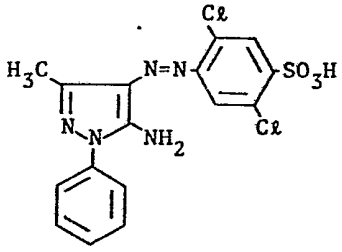
(I)

wherein R_1 represents a phenyl group, a substituted phenyl group (substituent: e.g. Cl, alkyl group, alkoxy group, sulfo group or carboxyl group), an alkyl group, or a substituted alkyl group (substituent: e.g. sulfo group or cyanoethyl group); R_2 represents an alkyl group, a phenyl group, a substituted phenyl group (substituent: e.g. C1, alkyl group or alkoxy group), a cyano group, a hydroxy group, an alkoxy group, an amino group, an acylamino group, an anilino group, a ureido group, an alkoxycarbonyl group, or a carbamoyl group; X represents a halogen atom, an alkyl group, or an alkoxy group; *n* represents 1, 2, 3, 4 or 5; and *m* represents 1, 2 or 3. When *m* is 1, R_1 is preferably a sulfosubstituted alkyl group or phenyl group.

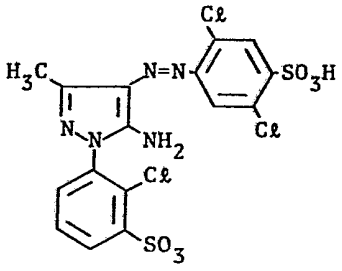
Practical examples of the preferred water-soluble yellow dyes are illustrated below.

Examples of Yellow Dye:

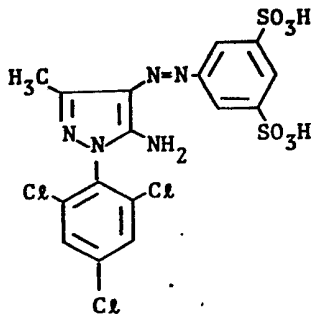
(Y-1)



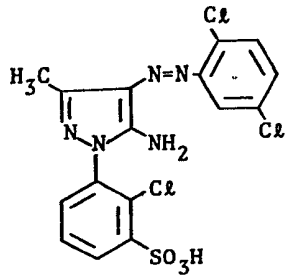
(Y-2)



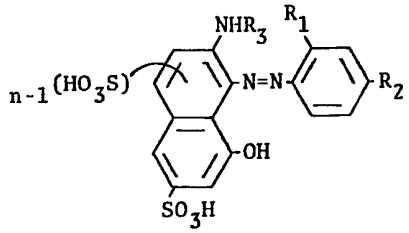
(Y-3)



(Y-4)



Preferred magenta dyes used in this invention are shown by formulæ (II), (III) and (IV). Formula (II) can be represented as follows:



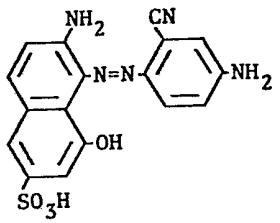
(II)

wherein R_1 represents a cyano group, an alkylsulfonyl group, an arylsulfonyl group, a trifluoromethyl group, or a trichloromethyl group; R_2 represents an amino group, an acylamino group, a substituyed ureido group, an alkyl-amino group, an alkoxy group, a substituted alkoxy group, or an alkyl group; R_3 represents a hydrogen atom or an alkyl group; and *n* represents 1 or 2.

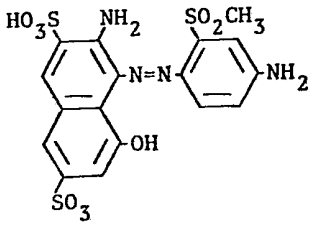
Practical examples of the water-soluble magenta dyes of formula (II) contained in the inks of this invention are illustrated below.

Examples of Magenta Dye:

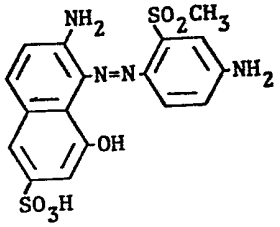
(M-1)



(M-2)

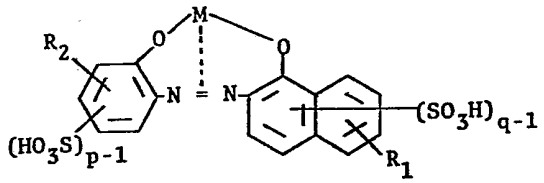


(M-3)



The foregoing magenta dyes used in this invention can be prepared as described in the specifications of Japanese Patent Applications (OPI) Nos. 89534/74 and 8630/79.

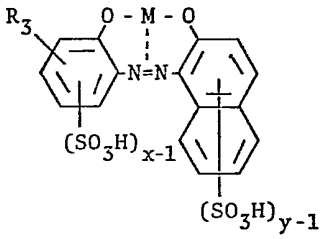
Formula (III) can be represented as follows:



(III)

wherein R_1 and R_2, which may be the same or different, each represents a hydrogen atom, a halogen atom (e.g., a chlorine or bromine atom), a lower alkyl group (e.g., methyl or ethyl group), a lower alkoxy group (e.g., methoxy or ethoxy group), an amino group, or a substituted amino group (substituent: acyl group, e.g., acetyl group, benzoyl group, methylsulfonyl group), a lower alkyl group (e.g., methyl or ethyl group), or an aryl group (e.g., phenyl group); p- represents 1, 2 or 3; q represents an integer of 1 to 4; $(p+q)$ represents 3, 4 and 5 and 6; and M represents Cu or Ni.

Formula (IV) can be represented as follows:

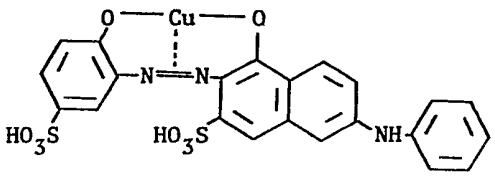


(IV)

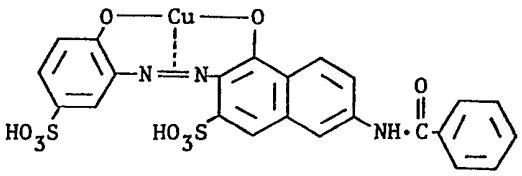
wherein R_3 represents a hydrogen atom, a halogen atom (e.g., chlorine or bromine atom), a lower alkyl group (e.g., methyl or ethyl group), or a lower alkoxy group (e.g., methoxy or ethoxy group); x represents 1, 2 or 3; y represents an integer of 1 to 4; $(x+y)$ represents 4, 5 or 6; and M represents Cu or Ni.

Practical examples of the water-soluble magenta dyes shown by formulæ (III) and (IV) are illustrated below.

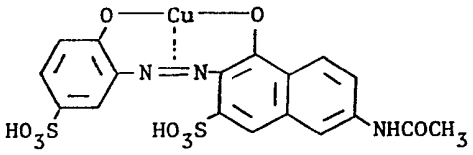
(M-4)



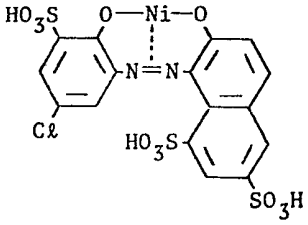
(M-5)



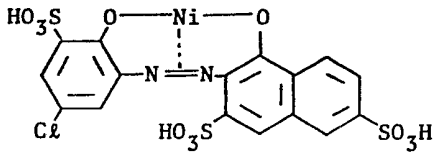
(M-6)



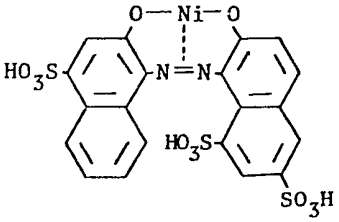
(M-7)



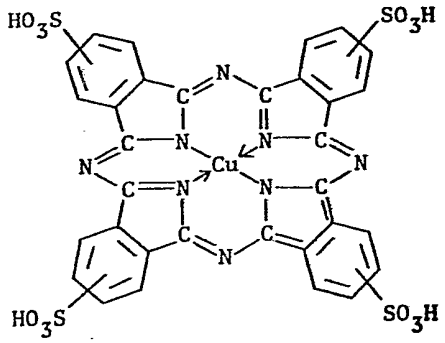
(M-8)



(M-9)



As cyan dyes, copper phthalocyanine tetrasulfonic acid, viz.,



or copper phthalocyanine disulfonic acid is preferably used in this invention.

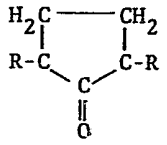
Copper phthalocyanine tetrasulfonic acid, which can also be used in this invention as a water soluble cyan dye, can be prepared by reacting copper phthalocyanine and chlorosulfonic acid to form copper phthalocyanine tetrasulfonic acid chloride, and pouring the chloride into water, as described in U.S. Patents 2,219,330, 3,305,559 and 3,082,201.

In addition, the sulfo group contained in the dyes shown by formulæ (I), (II), (III) and (IV) and copper phthalocyanine sulfonic acids may be an alkali metal salt thereof (e.g., a sodium or potassium salt) or an organic amine salt thereof (e.g., a triethylamine salt, a pyridine salt, a triethyanolamine salt, an ammonium salt).

As a black dye, C.I. Acid Black 155 is preferably used in this invention.

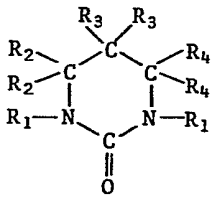
According to this invention, for forming multicolor recorded images having high color density and excellent color reproducibility, a combination of inks and a recording sheet is required, said inks properly distributing said dyes on the recording medium for absorbing light in desired spectral wavelength regions, reducing side absorptions as low as possible, and being stably jetted from nozzles of an ink jet recording device and said recording sheet have good absorptive property for the inks, and resulting in less spreading of the ink coloring components in the planar directions and less permeation into the inside of the sheet.

It is preferred that the inks meeting these characteristics contain a humectant. Preferred humectants used in this invention are the compounds shown by formulæ (V) to (VII) as follows:



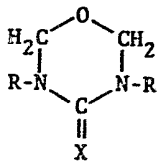
(V)

wherein R represents a hydroxyalkyl group or an alkoxyalkyl group;



(VI)

wherein R_1 represents a hydrogen atom, an alkyl group, or a substituted alkyl group; and R_2, R_3 and R_4, which may be the same or different, each represents a hydrogen atom, an alkyl group, a hydroxy group, or an alkxoy group; and

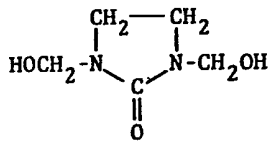


(VII)

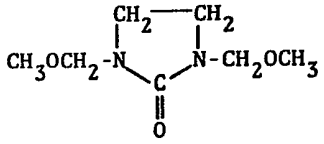
wherein R represents an alkyl group or a substituted alkyl group and X represents an oxygen atom or a sulfur atom.

Practical examples of the preferred compounds shown in formulæ (V) to (VII) used in this invention are illustrated below:

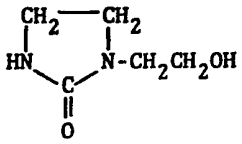
(V-1)



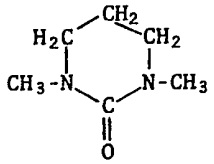
(V-2)



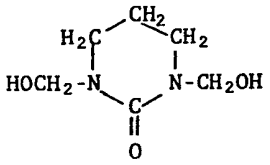
(V-3)



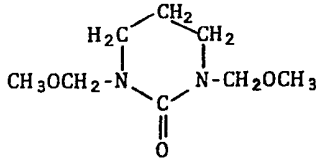
(VI-1)



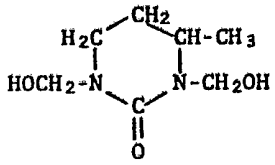
(VI-2)



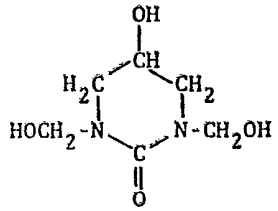
(VI-3)



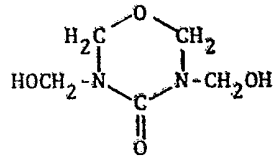
(VI-4)



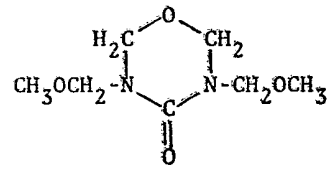
(VI-5)



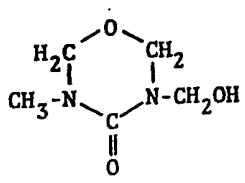
(VII-1)



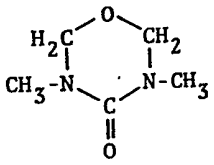
(VII-2)



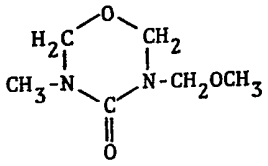
(VII-3)



(VII-4)



(VII-5)



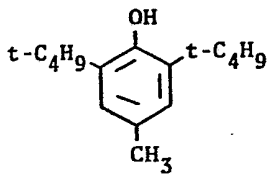
For use in this invention, a recording sheet suitable for forming multicolor recording images having excellent light resistance is a recording sheet having on the surface of the support a pigment-coated layer capable of adsorbing dyes of the foregoing inks and having coated thereon or containing therein a dye image fading preventing agent for preventing said dyes from being deteriorated by the action of ultraviolet rays and/or oxygen. The dye image fading preventing agent is coated on a pigment-coated layer formed on the surface of the support, that is, is coated on the side onto which ink jet printing is to be applied, or is coated on the support together with pigment.

According to this invention, as the dye image facing preventing agent, a phenolic fading preventing agent is preferably used and greatly improves the fastness of ink jet multicolor recorded images to light. Examples of compounds useful as the phenolic fading preventing agent include phenol derivatives wherein a least one of the ortho-positions with respect to the hydroxy group is substituted by a tertiary alkyl group, bisphenol derivatives, compounds having a phenol derivative at a part of phosphoric acid ester, and phenol compounds wherein the *p*-position with respect to the hydroxy group is substituted by an oxygen atom forming part of a 5- or 6-membered ring which is fused together with the phenol nucleus to form a condensed ring compound.

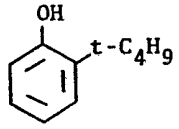
Practical examples of preferred compounds used as phenolic fading preventing agents in this invention are illustrated below.

(1) Practical examples of phenol derivatives wherein at least one of the ortho-positions with respect to the hydroxy group is substituted by a tertiary alkyl group:

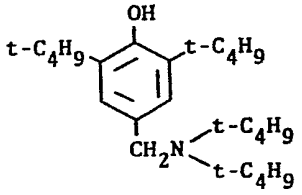
(A-1)



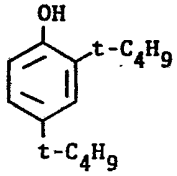
(A-2)



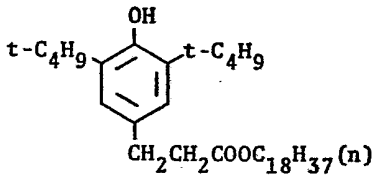
(A-3)



(A-4)

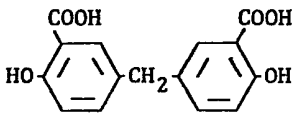


(A-5)

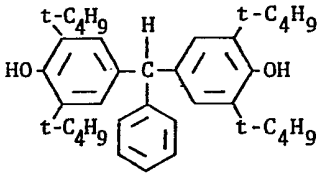


(2) Practical examples of the bisphenol derivatives:

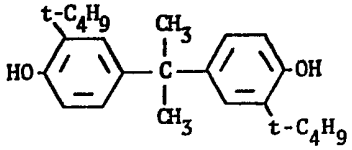
(A-6)



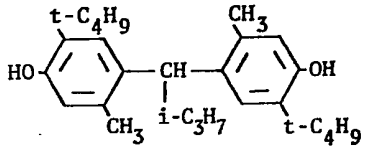
(A-7)



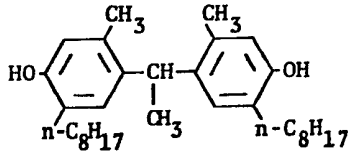
(A-8)



(A-9)

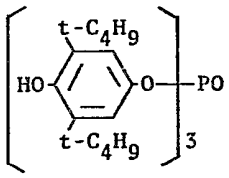


(A-10)

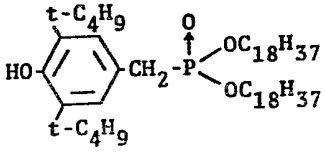


(3) Practical examples of the phosphoric acid esters:

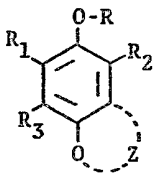
(A-11)



(A-12)



Phenol derivatives wherein the p-position with respect to the hydroxy group is substituted by an oxygen atom forming part of a 5– or 6–membered ring forming a condensed nucleus together with the phenol nucleus include compounds shown by formula (VIII), viz.,

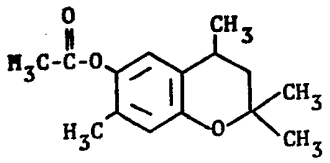


(VIII)

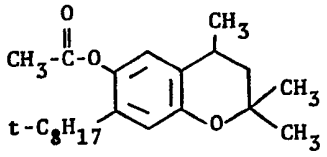
wherein R represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted cycloalkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, $R_4CO–$, $R_5SO_2–$, or $R_6NHCO–$ (wherein R_4, R_5 and R_6 each represents a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted cycloakyl group, a substituted or unsubstituted aryl group, or a substituted or unsubstituted aralkyl group); R_1, R_2 and R_3 each represents a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkylthio group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aryloxy group, a substituted or unsubstituted arylthio group, a substituted or unsubstituted acyl group, a substituted or unsubstituted acylamino group, a substituted or unsubstituted acyloxy group, a substituted or unsubstituted sulfonamido group, a substituted or unsubstituted alkylamino group, a substituted or unsubstituted cycloalkyl group, or a substituted or unsubstituted alkoxy-carbonyl group; and Z represents an atomic group necessary for forming a chroman ring or coumaran ring; said chroman ring or courmaran ring may be substituted by a halogen atom, alkyl group, alkylthio group, alkoxy group, alkenyl group, alkenyloxy group, aryl group, aryloxy group, N-substituted amino group, heterocyclic group, or a residue forming a condensed ring.

Practical examples of the foregoing compounds shown by formula (VIII) are illustrated below:

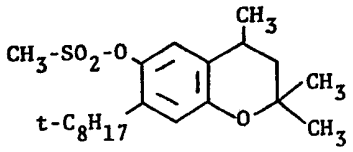
(VIII-1)



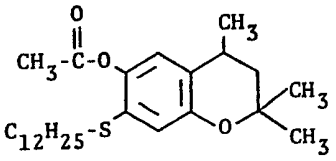
(VIII-2)



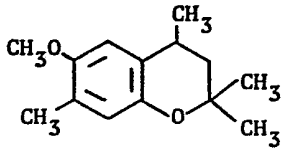
(VIII-3)



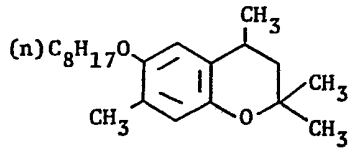
(VIII-4)



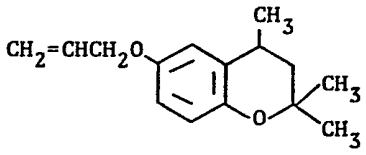
(VIII-5)



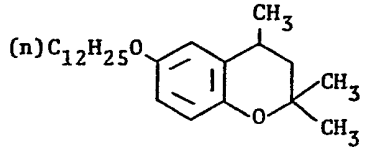
(VIII-6)



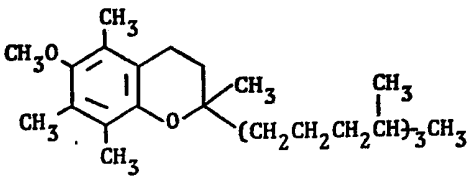
(VIII-7)



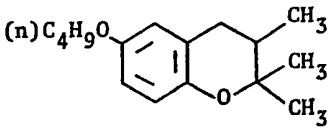
(VIII-8)



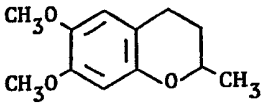
(VIII-9)



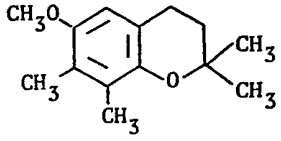
(VIII-10)



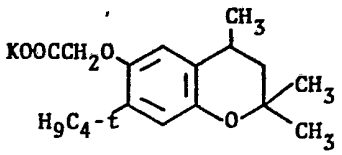
(VIII-11)



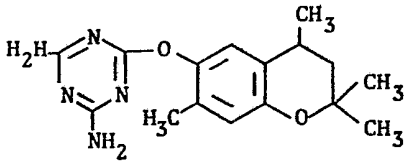
(VIII-12)



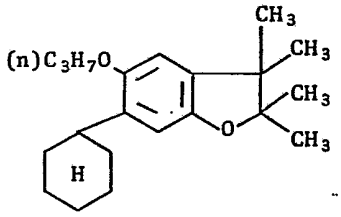
(VIII-13)



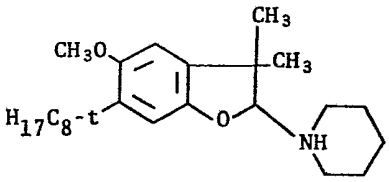
(VIII-14)



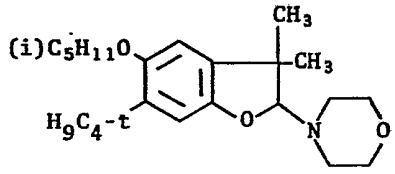
(VIII-15)



(VIII-16)



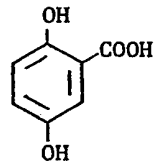
(VIII-17)



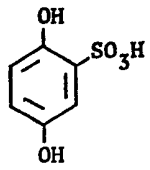
Compounds according to formula (VIII) can be prepared by methods as described in U.S. Patents 3,432,300, 3,547,627 and 3,573,050, Japanese Patent Publication No. 20977/74, and Japanese Patent Applications (OPI) Nos. 147433/77, 17729/78, 20327/78, 52421/78 and 77527/78.

According to this invention, the fading preventing effect of the dye images is further improved by using the dye image fading preventing agent together with the hydroquinone series antioxidant described below.

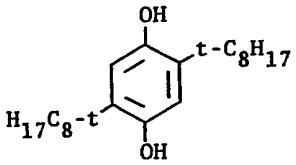
(B-1)



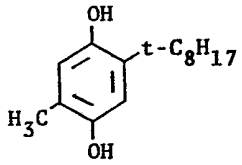
(B-2)



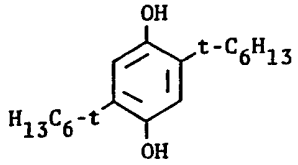
(B-3)



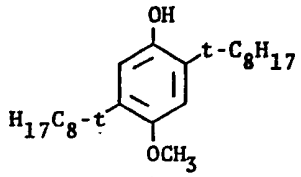
(B-4)



(B-5)

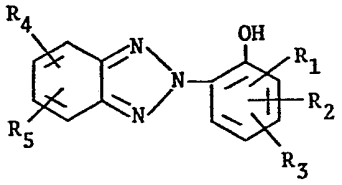


(B-6)



Furthermore, according to this invention, the effect of preventing fading and discoloring of the dye images and the non-imaged portions is greatly improved by using an ultraviolet absorbent together with the dye image fading preventing agent.

The ultraviolet absorbents preferably used in this invention are non-diffusible 2-hydroxphenyl-substituted benzotriazole series compounds shown by formula (IX), viz.,



(IX)

wherein R_1, R_2, R_3, R_4 and R_5 each represents a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an alkoxy group, a carbalkoxy group, an aryl group or a aryloxy group.

Some of the hydroxybenzotriazole series ultraviolet absorbents are commercially available, and hydroxybenzotriazoles may be also prepared by the methods described in Japanese Patent Publications Nos. 10466/61 and 26187/67.

Practical examples of the compounds shown in formula (IX) are listed below:

(IX–1) 2-(2′-hydroxy-5′-methylphenyl)benzoytriazole,
(IX–2) 2-(2′-hydroxy-3′,5′-di-t-butylphenyl)benzotriazole,
(IX–3) 2-(2′-hydroxy-3′,5′-di-t-butylphenyl)-5-chlorobenzotriazole,
(IX–4) 2-(2′-hydroxy-5′-t-butylphenyl)benzotriazole,
(IX–5) 2-(2′-hydroxy-5′-t-butylphenyl)-5-chlorobenzotriazole,
(IX–6) 2-(2′-hydroxy-3′-sec-butyl-5′-t-butylphenyl)-benzotriazole,
(IX–7) 2-(2′-hydroxy-3′-sec-butyl-5′-t-butylphenyl)-5-chlorobenzotriazole,
(IX–8) 2-(2′-hydroxy-4′-n-hexyloxyphenyl)benzotriazole,
(IX–9) 2-(2′-hydroxy-5′-issocytlphenyl)benzotriazole,
(IX–10) 2-(2′-hydroxy-3′,5′-di-t-amylphenyl)benzotriazole, and
(IX–11) 2-(2′-hydroxy-5′-isooctylphenyl)-5′-methyl-benzotriazole.

The dye image fading preventing agent, the hydroquinone series antioxidant, and the ultraviolet absorbent used in this invention are incorporated in an aqueous hydrophilic colloid coating solution used for forming a coating layer formed on the surface of a support to absorb the coloring components, or are incorporated in a hydrophilic colloid layer associated with the coating layer by using a solvent dispersion technique.

The dye image fading preventing agent, the hydroquinone antioxidant, and the ultraviolet absorbent of formula (IX) are dissolved in a high-boiling water-immiscible organic solvent, a low-boiling organic solvent, a water-soluble organic solvent, or a mixture of a water-immiscible high-boiling organic solvent and/or a low-boiling organic solvent and/or a water-soluble organic solvent, and then the solvent solution is dispersed in an aqueous solution of gelatin or other hydrophilic colloid.

The high-boiling water-immiscible organic solvents described in U.S. Patent 2,322,027 can be used as the solvent in this invention.

Typical examples of the high-boiling organic solvents useful in this invention include di-*n*-butyl phthalate, benzyl phthalate, triphenyl phosphate, tri-o- cresyl phosphate, diphenyl-mono-*p*-*t*-butylphenyl phosphate and tri-p-*t*-butylphenyl phosphate.

According to a preferred embodiment of the invention, the pigment coated on the recording sheet is selected from zeolite, vermiculite, kaolinite, halloysite, acid-treated halloysite, attapulgite, diatomaceous earth, silicic acid ahydride, aluminum silicate, calcium silicate and magnesium silicate.

When adhesives for absorbing dyes are used as dye absorbing adhesives for pigment, the effect of this invention is increased. Examples of such dye absorbing adhesives used in this invention are sodium polyacrylate, styrene-maleic anhydride copolymer sodium salt, methyl vinyl ether-maleic anhydride copolymer, ethylene-maleic anhydride copolymer, polystyrene sulfonate, carboxymethyl cellulose, cellulose sulfate, carboxy-denatured polyvinyl alcohol, sodium alginate, gum arabic, polyethyleneimine, polyamide-polyamine resin, cationic starch, casein, soybean protein, acrylic acid-dimethylaminoethyl methacrylate copolymer and an acrylic acid ester copolymer emulsion having a cationic dissociation group.

Other components that can be used in pigment-coated layers in this invention include starch, polyvinyl alcohol, methyl cellulose, hydroxyethyl cellulose, hydroxyethylated starch, polyacrylam-

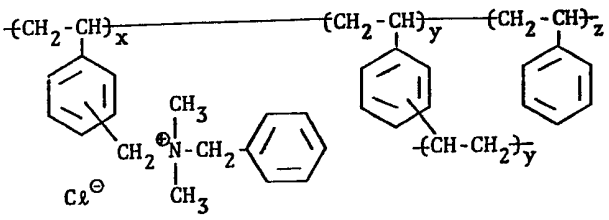
ide, polyvinyl-pyrrolidone or a basic latex polymer.

When an ink jet recording is applied onto the ink jet recording sheet containing a basic polymer latex according to this invention by aqueous inks containing direct dyes or acid dyes having anionic dissociation group, the dyes in the aqueous inks ionically bond to the basic polymer latex in the recording sheet to thereby insolubilize the dyes, and thus the dissolution of the dyes is completely prevented.

Since the basic polymer latex is water-insoluble and has a strong mordanting power for dyes, the water resistance of the ink jet recorded image becomes complete, and thus even when the ink jet recorded images are wetted with water or immersed in water for a long period of time, no change is observed in the image.

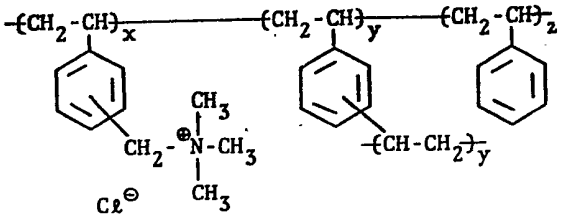
Practical examples of basic latex polymers useful in this invention are shown below:

(P-1)



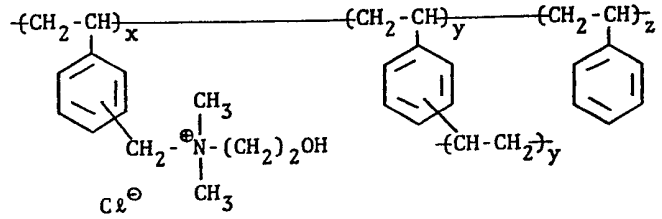
x:y:z = 49:2:49

(P-2)



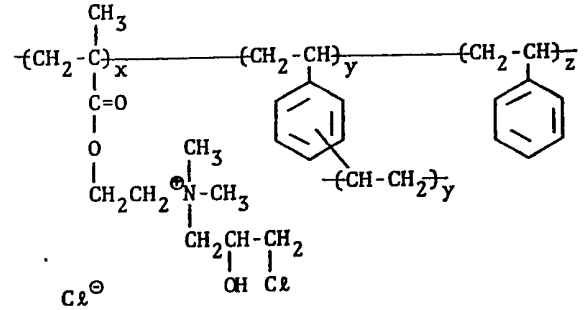
x:y:z = 49:2:49

(P-3)



x:y:z = 49:2:49

(P-4)



x:y:z = 48:4:48

The invention will be explained in further detail by the following examples.

EXAMPLE 1

Samples were prepared by coating one surface of a base paper (basis weight: 100 g/m^2) that had been sized (25 g/m^2) with a mixed suspension of a solution of a dye image fading preventing agent, a dye image fading preventing agent and a hydroquinone series antioxidant; or a dye image fading preventing agent, a hydroquinone series antioxidant, and an ultraviolet absorbent, and a pigment dispersion.

That is, the fading preventing agent and other components as shown in Table 1 were dissolved in a mixture of a high-boiling organic solvent and a low-boiling organic solvent at 65°C and after dispersing the solution by emulsification in 30 ml of an aqueous solution of 10% by weight gelatin containing saponin by means of a colloid mill, 15 ml of water was added to the emulsion followed by mixing. The resulting emulsion was mixed with a suspension containing 5% by weight gelatin, 1.5% by weight hydroxyethyl cellulose, 7% by weight synthetic aluminum silicate, and 0.5% by weight polyamine-polyamide-epichlorohydrin resin as a hardening agent by means of a colloid mill, and the resultant suspension was coated on one surface of the foregoing base paper to obtain a dry solid coverage of 8 g/m^2 by means of an air knife coater, and the sheet thus coated was calendered. Thus, ink jet recording sheet Samples 1 to 9 were prepared. (Sample 1 was, however, a comparison sample containing no compounds required in this invention.)

Onto each of the recording sheet Samples 1 to 9 thus obtained were jetted four aqueous colored inks, viz., yellow, magenta, cyan, and black by means of a multicolor ink jet printer having four ink jet nozzles, to obtain monochromatic recordings and from 2 to 4 colored recordings.

After measuring the densities of yellow, magenta, cyan and black images and the density of stain in the non-imaged portion (measured at yellow density) of each sample by means of a Macbeth reflection densitometer RD–514, the sample was subjected to a sum exposure test. That is, each sample was exposed to the direct rays of the sun at an angle of 45° to the southern direction for 7 days. After exposure, the density of each color and the yellow density of the non-imaged portion were measured again and the percentage ratio ($D/D_0 \times 100$) of the density (D) after exposure to the density (D_0) before exposure was determined, which was defined as a fading ratio. The results are shown in Table 1. "Macbeth" is a registered Trade Mark.

TABLE 1

Sample No.	Fading Preventing Agent and Amount (g)	Hydroquinone Series Antioxidant and Amount (g)	Ultraviolet Absorbent and Amount (g)	High-Boiling Solvent and Amount (cc)	Low-Boiling Solvent and Amount (cc)
1 (Comparison)	None	None	None	TCP 0.8	EA 9.0
2 (Invention)	(VIII-1) 1.3	None	(IX-2) 0.2	"	"
3 (Invention)	(VIII-6) 1.4	None	(IX-2) 0.3	"	"
4 (Invention)	(VIII-19) 1.1	(B-3) 0.1	(IX-2) 0.3	"	"
5 (Invention)	(VIII-32) 1.3	None	(IX-3) 0.2	"	"
6 (Invention)	(VIII-5) 1.0	(B-5) 0.2	(IX-5) 0.3	TCP 1.0	EA 10.0
7 (Invention)	(VIII-20) 1.6	None	None	TCP 0.8	EA 9.0
8 (Invention)	(VIII-19) 1.6	None	None	"	"
9 (Invention)	(VIII-27) 1.6	None	None	DBP 1.0	MA 9.0

DBP: dibutyl phthalate, TCP: tri-o-cresylphosphate, EA: ethyl acetate,
MA: methyl acetate

TABLE 1
(cont'd)

Sample No.	Fading Rate ($D/D_0 \times 100$) Yellow (%)	Magenta (%)	Cyan (%)	Black (%)	Stain Density Before Exposure	After Exposure
1 (Comparison)	91	62	80	90	0.02	0.15
2 (Invention)	96	91	93	94	0.03	0.05
3 (Invention)	96	92	94	95	0.03	0.04
4 (Invention)	98	93	95	96	0.03	0.06
5 (Invention)	95	92	93	93	0.02	0.04
6 (Invention)	97	93	95	97	0.03	0.05
7 (Invention)	94	90	91	92	0.03	0.06
8 (Invention)	93	89	91	92	0.03	0.05
9 (Invention)	94	90	91	93	0.03	0.05

As is clear from the results shown in Table 1, Samples 2 to 9 of this invention showed greatly restrained fading of yellow, magenta, cyan and black inks and strain density as compared to Sample 1, containing no compounds of this invention.

The yellow, magenta, cyan and black aqueous inks used in the example were obtained by stirring the composition shown below for 1 hour while heating to 50 to 60°C, and then filtering the composition under pressure by means of a 0.8 micron microfiller (FM type, made by Fuji Photo Film Co., Ltd.).

Yellow Ink:

	wt. parts
Dye [yellow dye (Y-1)]	3.0
N,N-Dimethoxymethyl-2(1H)-pyrimidinone [(VI-3)]	20.0
Noigen P (polyethylene glycol alkyl ether; made by Dai-Ichi-Kogyo Seiyaku Co., Ltd.)	0.1
Triethanolamine	5.0
Water	71.9

Magenta Ink:

	wt. parts
Dye [magenta dye (M-2)]	1.5
N,N-Dimethoxymethyl-urone [(VII-2)]	20.0
Noigen P	0.1
Diethylene glycol monoethyl ether	0.5
Triethanolamine	1.0
Water	76.9

Cyan Ink:

	wt. parts
Dye (copper phthalocyanine tetrasulfonic acid sodium salt)	2.4
N,N'-Dimethoxymethyl-imidazolidinone [(V-2)]	20.0
Diethylene glycol monobutyl ether	0.5
Diethylene glycol	1.5
Noigen P	0.1
Triethanolamine	2.0
Water	73.5

Black Ink:

	wt. parts
Dye (C.I. Acid Black 155)	3.0
N,N'-Dimethoxymethyl-imidazolidinone [(V-2)]	20.0
2,2'-Thiodiethanol	10.0
Noigen P	0.1
Diethylene glycol monoethyl ether	1.0
Triethanolamine	2.0
Water	63.9

EXAMPLE 2

One surface of a base paper (basis weight: 150 g/m^2) that had been sized (25 g/m^2) was coated with a suspension containing 5% by weight gelatin, 1.5% by weight hydroxyethyl cellulose, basic latex polymer (as shown in Table 2) and 5% by weight diatomaceous earth at a dry solid coverage of 80 g/m^2 by means of an air knife coater.

After dissolving the fading preventing agent (as shown in Table 2) in a mixture of 0.8 ml of tri-o-cresyl-phosphate and 9 ml of ethyl acetate at 65°C, the solution was dispersed by emulsification in 30 ml of an aqueous solution of 10% by weight gelatin containing saponin by a colloid mill, the emulsion was rinsed with 30 ml of water, cooled, noodled, and dried. The dried material was re-dispersed in a solution containing 30 ml of 6% by weight gelatin, 4 ml of 7.5% by weight saponin, and 50 ml of water.

The resulting dispersion was overcoated on the foregoing pigment layer formed on the base paper at a dry solid coverage of 2.5 g/m^2 by means of an air knife coater, and the coated sheet was calendered. Thus, ink jet recording sheet Samples 10 to 14 were prepared. (Sample 10 was, however, a comparison sample containing no fading preventing agent of this invention).

For these samples, ink jet printing, sun exposure, and reflection density measurement as in Example 1 were applied, and the extent of the water resistance of the recorded images was measured by the following method. Particularly, the reflection density of the sample ink jet printed with the cyan ink was measured, and then the sample was immersed in running water for 1 hour. After withdrawing the sample and drying it, the cyan reflection density was measured and the ratio of the value to the reflection density before immersion in water was expressed as a percentage, which was defined as the waterproofing ratio hereinbefore. The results are shown in Table 2.

TABLE 2

Sample No.	Fading Preventing Agent and Amount (g)	Hydroquinone Series Antioxidant and Amount (g)	Ultraviolet Absorbent and Amount (g)	High-Boiling Solvent and Amount (cc)	Low-Boiling Solvent and Amount (cc)	Basic Latex Polymer and Amount (g)
10 (Comparison)	None	None	None	TCP 0.8	EA 9.0	None
11 (Invention)	(VIII-1) 1.3	None	(IX-2) 0.2	"	"	(P-2) 4
12 (Invention)	(VIII-19) 1.1	(B-3) 0.1	(IX-2) 0.3	"	"	"
13 (Invention)	(VIII-5) 1.0	None	(IX-5) 0.5	"	"	(P-9) 4
14 (Invention)	(VIII-5) 1.0	(B-5) 0.1	(IX-5) 0.4	"	"	"

TABLE 2
(cont'd)

Sample No.	Fading Rate ($D/D_0 \times 100$) Yellow (%)	Magenta (%)	Cyan (%)	Black (%)	Stain Density Before Exposure	Stain Density After Exposure	Waterproofing Ratio (cyan) (%)
10 (Comparison)	91	62	80	90	0.02	0.15	26
11 (Invention)	95	90	93	93	0.03	0.05	99
12 (Invention)	96	92	95	96	0.03	0.06	100
13 (Invention)	95	91	94	95	0.02	0.04	99
14 (Invention)	98	93	94	97	0.02	0.05	98

As is clear from the results shown in Table 2, Samples 11 to 14 of this invention shows greatly restrained fading ratios of yellow, magenta, cyan and black inks, and showed little stain density as compared to Comparison Sample 10, which contained no fading preventing agent of this invention. Moreover, the water resistance of the recorded images in the samples of this invention was greatly increased by the use of basic latex polymers. Thus, the water resistance and light fastness of the ink jet recorded images can be increased by the invention.

CLAIMS

1. A process for forming ink jet recording images comprising applying ink jet printing on a recording sheet containing a dye image fading preventing agent using at least one aqueous ink jet printing ink comprising a water-soluble acid dye or water-soluble direct dye.

2. A process as in Claim 1, wherein said aqueous ink jet printing ink is an aqueous yellow, magenta, cyan, or black ink jet printing ink.

3. A process as in Claim 1 or 2, wherein said recording sheet contains the dye image fading preventing agent in a pigment-coated layer formed thereon.

4. A process as in Claim 1, 2, or 3, wherein the dye image fading preventing agent is a phenol derivative wherein at least one of the ortho-positions with respect to the hydroxy group is substituted by a tertiary alkyl group.

5. A process as in Claim 1, 2, or 3, wherein the dye image fading preventing agent is a bisphenol derivative.

6. A process as in Claim 1, 2, or 3, wherein the dye image fading preventing agent is a compound having a phenol derivative as a part of a phosphoric acid ester.

7. A process as in Claim 1, 2, or 3, wherein the dye image fading preventig agent is a phenol compound wherein the *p*-position with respect to the hydroxy group is substituted by an oxygen atom forming part of a 5– or 6–membered ring which is fused together with the phenol nucleus to form a condensed ring compound.

8. A process as claimed in Claim 3 or any of Claims 4 to 7 dependent thereon, wherein the pigment is selected from zeolite, vermiculite, kaolinite, halloysite, acid-treated halloysite, attapulgite, diatomaceous earth, silicic acid anhydride, aluminum silicate, calcium silicate and magnesium silicate.

9. A process as claimed in any preceding claim, wherein the ink contains any of the dyes Y-1 to Y-4, M-1 to M-9 or copper phthalocyanine dyes shown hereinbefore.

10. A process as claimed in any preceding claim, wherein the fading prevention agent is any of the compounds A-1 to A-12 or VIII-1 to VIII-7 shown hereinbefore.

11. A process as claimed in Claim 1 for forming an ink jet recorded image, substantially as hereinbefore described with reference to any of Samples 2 to 9 or 11 to 14 of the Examples.

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