(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 170 145 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.01.2002 Bulletin 2002/02

(51) Int Cl.[7]: **B41M 5/00**

(21) Application number: **01202336.2**

(22) Date of filing: **18.06.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **06.07.2000 US 610736**
06.07.2000 US 611123

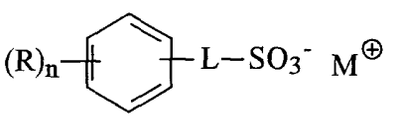
(71) Applicant: **EASTMAN KODAK COMPANY**
Rochester, New York 14650 (US)

(72) Inventor: **Merkel, Paul B.**
Rochester, New York 14650-2201 (US)

(74) Representative:
Nunney, Ronald Frederick Adolphe et al
Kodak Limited, Patent Department (W92)-3A,
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)

(54) Ink jet recording element and printing method

(57) An ink jet recording element comprising a substrate having thereon an image-receiving layer comprising a polymeric mordant and a polymeric binder containing a stabilizer having the following formula:



wherein:

each R individually represents a substituted or unsubstituted alkyl or alkoxy group having from 1 to 7 carbon atoms; a phenyl group having from 6 to 10 carbon atoms; a phenoxy group having from 6 to 10 carbon atoms; a carbonamido group having from 1 to 8 carbon atoms; or two or more R groups can be combined together to form a ring structure;
n is 1 to 4;
L is a linking group containing at least one carbon atom; and
M^+ is a monovalent cation;

with the proviso that the total number of carbon atoms in all the R's and L taken together is at least 3, and at least one R is the alkoxy group.

EP 1 170 145 A2

Description

[0001] This invention relates to an ink jet recording element and printing method. More particularly, this invention relates to an ink jet recording element containing a stabilizer and a printing method using the element.

[0002] In a typical ink jet recording or printing system, ink droplets are ejected from a nozzle at high speed towards a recording element or medium to produce an image on the medium. The ink droplets, or recording liquid, generally comprise a recording agent, such as a dye or pigment, and a large amount of solvent. The solvent, or carrier liquid, typically is made up of water, an organic material such as a monohydric alcohol, a polyhydric alcohol or mixtures thereof.

[0003] An ink jet recording element typically comprises a support having on at least one surface thereof an ink-receiving or image-forming layer, and includes those intended for reflection viewing, which have an opaque support, and those intended for viewing by transmitted light, which have a transparent support.

[0004] While a wide variety of different types of image-recording elements for use with ink jet devices have been proposed heretofore, there are many unsolved problems in the art and many deficiencies in the known products which have limited their commercial usefulness.

[0005] It is well known that in order to achieve and maintain photographic-quality images on such an image-recording element, an ink jet recording element must:

- Be readily wetted so there is no puddling, i.e., coalescence of adjacent ink dots, which leads to non-uniform density
- Bind dye with sufficient strength to minimize both water washout and high- humidity smearing
- Exhibit no image bleeding
- Exhibit the ability to absorb high concentrations of ink and dry quickly to avoid elements blocking together when stacked against subsequent prints or other surfaces
- Exhibit no discontinuities or defects due to interactions between the support and/or layer(s), such as cracking, repellencies, comb lines and the like
- Not allow unabsorbed dyes to aggregate at the free surface causing dye crystallization, which results in bloom or bronzing effects in the imaged areas
- Have an optimized image fastness to avoid fade from contact with water or radiation by daylight, tungsten light, or fluorescent light

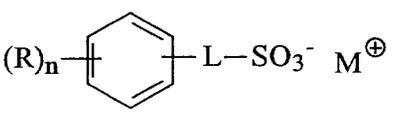
[0006] An ink jet recording element that simultaneously provides an almost instantaneous ink dry time and good image quality is desirable. However, given the wide range of ink compositions and ink volumes that a recording element needs to accommodate, these requirements of ink jet recording media are difficult to achieve simultaneously.

[0007] U.S. Patent 5,688,633 relates to an ink for ink jet printing containing a stabilizer. However, there is a problem with providing a stabilizer in an ink in that more of the stabilizer would be required and there may be interactions between the stabilizer and other components of the ink.

[0008] EPA 882 600 discloses an ink jet system containing a stabilizer. However, the stabilizers of the present invention are not disclosed.

[0009] It is an object of this invention to provide an ink jet recording element that contains a stabilizer which can be used with a variety of ink jet inks. It is another object of this invention to provide an ink jet recording element that has good light stability for a dye image transferred to it. It is another object of the invention to provide a printing method using the above described element.

[0010] These and other objects are achieved in accordance with the invention which comprises an ink jet recording element comprising a substrate having thereon an image-receiving layer comprising a polymeric mordant and a polymeric binder containing a stabilizer having the following formula:



wherein:

each R individually represents a substituted or unsubstituted alkyl or alkoxy group having from 1 to 7 carbon atoms, such as methyl, t-butyl, benzyl, hydroxyethyl, methoxy, ethoxy or t-butoxy; a phenyl group having from 6 to 10 carbon atoms, such as phenyl or p-tolyl; a phenoxy group having from 6 to 10 carbon atoms, such as phenoxy or m-methylphenoxy; a carbonamido group having from 1 to 8 carbon atoms, such as N-methylacetamido or propionamido; or two or more R groups can be combined together to form a ring structure, such as methylenedioxy or

ethylenedioxy;
n is 1 to 4;
L is a linking group containing at least one carbon atom, such as methylene, ethylene, propylene, ethyleneoxy, propyleneoxy or phenylethylene; and
M^+ is a monovalent cation, such as Na^+, K^+ or NH_4^+; with the proviso that the total number of carbon atoms in all the R's and L taken together is at least 3, and at least one R is the alkoxy group.

[0011] The ink jet recording element of the invention provides a strong ink binding and good image quality.

[0012] Another embodiment of the invention relates to an ink jet printing method comprising the steps of:

A) providing an ink jet printer that is responsive to digital data signals;

B) loading the printer with an ink jet recording element as described above;

C) loading said printer with an ink jet composition; and

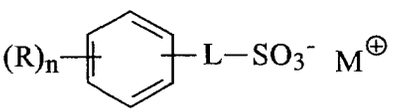
D) printing on said ink jet recording element using said ink jet ink in response to said digital data signals.

[0013] The substrate used in the invention may be porous such as paper or nonporous such as resin-coated paper; synthetic paper, such as Teslin® or Tyvek®; an impregnated paper such as Duraform®; cellulose acetate or polyester films. The surface of the substrate may be treated in order to improve the adhesion of the image-receiving layer to the support. For example, the surface may be corona discharge treated prior to applying the image-receiving layer to the support. Alternatively, an under-coating or subbing layer, such as a layer formed from a halogenated phenol or a partially hydrolyzed vinyl chloride-vinyl acetate copolymer, can be applied to the surface of the support.

[0014] The polymeric binder that is used in the image-recording layer of the invention, can be, e.g., a water soluble polymer such as poly(vinyl alcohol), gelatin, poly(vinyl pyrrolidone), poly(2-ethyl-2-oxazoline), poly(2-methyl-2-oxazoline), poly(acrylamide), Chitosan, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, etc. Other binders can also be used such as low T_g polymer latexes such as poly(styrene-co-butadiene), a polyurethane latex, a polyester latex, poly(n-butyl acrylate), poly(n-butyl methacrylate), poly(2-ethylhexyl acrylate), a copolymer of n-butylacrylate and ethylacrylate, a copolymer of vinylacetate and n-butylacrylate, etc.

[0015] Other additives may also be included in the image-recording layer such as pH-modifiers like nitric acid, cross-linkers, rheology modifiers, surfactants, UV-absorbers, biocides, lubricants, dyes, dye-fixing agents or mordants, optical brighteners etc.

[0016] In a preferred embodiment of the invention, L in the above formula contains at least one methylene group. In another preferred embodiment, the stabilizer contains at least two alkoxy groups. In another preferred embodiment the total number of carbon atoms in the R's and L taken together is a least 4. Following are examples of stabilizers which can be used in the invention:

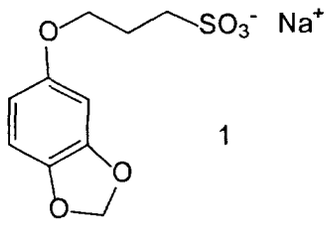


Stabilizer	R	n	L	M
1	3,4-methylenedioxy	2 (ring)	1-(propyleneoxy-3-sulfonate)	Na
2	2-t-butyl 4-methoxy	2	1-(propyleneoxy-3-sulfonate)	Na
3	2,5-dimethoxy	2	1-(ethylene-2-(phenyl-4-sulfonate))	Na
4	2,4,5-trimethoxy	3	1-(ethylene-2-(phenyl-4-sulfonate))	Na
5	2-t-butyl 4-methoxy	2	1-(propyleneoxy-3-sulfonate)	K
6	3,4-methylenedioxy	2 (ring)	1-(propyleneoxy-3-sulfonate)	NH_4
7	2,4,5-trimethoxy	3	1-(ethylene-2-sulfonate)	K

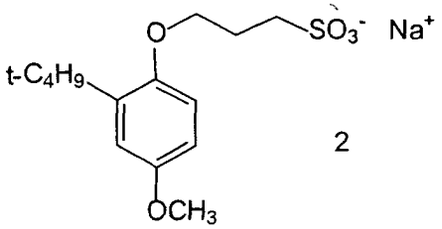
(continued)

Stabilizer	R	n	L	M
8	2-methoxy 4-phenoxy	2	1-(propyleneoxy-3-sulfonate)	Cs
10	2-methoxy 4-N-ethylacetamido	2	1-(ethyleneoxy-2-(ethyleneoxy-2-sulfonate))	K
11	2,5-dimethyl 4-ethoxy	3	1-(butylene-4-sulfonate)	Na
12	4-t-butoxy	1	1-(propyleneoxy-3-sulfonate)	Na

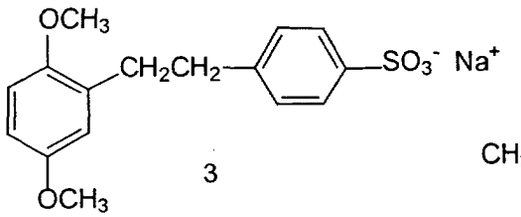
[0017] Structures of stabilizers 1-4 and 10 are drawn below for clarity:



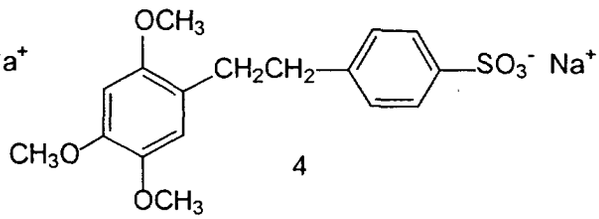
1



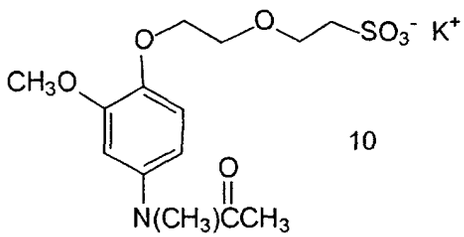
2



3



4



10

[0018] The benzene ring of the stabilizer may contain electron-donating substituents, such as alkyl and alkoxy groups, to enhance its efficiency as a quencher of excited states and as a stabilizer toward light-induced dye fading. One commonly-used measure of electron-donating character is provided by Hammett sigma values, which are published, for example, in "Exploring QSAR, Hydrophobic, Electronic and Steric Constants", C. Hansch, A. Leo and D. Hoekman, American Chemical Society, 1995. Electron-donating groups generally have negative Hammett sigma values. In a preferred embodiment of this invention, the sum of the Hammett sigma values of the R groups (referenced to the position of attachment of L) is less than -0.10

[0019] The stabilizer of this invention is coated in the ink jet recording element of this invention at a level of from 0.04 to 1.6 g/m^2, and preferably from 0.08 to 0.8 g/m^2.

[0020] Any polymeric mordant can be used in the invention. In a preferred embodiment, the mordant can be a cationic mordant, such as a protonated amine-containing polymer or a polymer which contains a quaternary ammonium group. Examples of these mordants include poly(1-vinylimidazole), poly(4-vinylpyridine), poly(styrene-co-N-benzyl-N,N-dimethyl-N-vinylbenzyl-ammonium chloride-co-divinylbenzene) (99:99:2 mole ratio), poly(N,N,N-tributyl-N-vinylbenzyl-ammonium chloride), poly(N,N-dimethyl-N-benzyl-N-vinylbenzyl-ammonium chloride), poly(styrene-co-N,N,N-trimethyl-N-vinylbenzyl-ammonium chloride) (1:1 mole ratio), poly(N,N,N-trimethyl-N-vinylbenzyl-ammonium chloride-co-

divinylbenzene) (87:13 mole ratio), poly(N,N-dimethyl-N-octadecyl-N-vinylbenzyl-ammonium chloride), poly(styrene-co-1-vinylimidazole-co-3-hydroxyethyl-1-vinylimidazolium chloride) (5:4:1 mole ratio), poly(styrene-co-1-vinylimidazole-co-3-benzyl-1-vinylimidazolium chloride) (5:4:1 mole ratio), poly(styrene-co-1-vinylimidazole-co-3-hydroxyethyl-1-vinylimidazolium chloride) (2:2:1 mole ratio), poly(styrene-co-4-vinylpyridine-co-1-hydroxyethyl-4-vinylpyridinium chloride) (5:4:1 mole ratio), poly(diallydimethylammonium chloride) and chitosan.

[0021] The mordant in the ink jet recording element of this invention may be coated at a level of from 0.08 to 4.0 g/m^2, or more typically from 0.15 to 2.0 g/m^2.

[0022] The ink jet coating may be applied to one or both substrate surfaces through conventional pre-metered or post-metered coating methods such as blade, air knife, rod, roll coating, etc. The choice of coating process would be determined from the economics of the operation and in turn, would determine the formulation specifications such as coating solids, coating viscosity, and coating speed.

[0023] The image-receiving layer thickness may range from 1 to 60 μm, preferably from 5 to 40 μm.

[0024] After coating, the ink jet recording element may be subject to calendering or supercalendering to enhance surface smoothness. In a preferred embodiment of the invention, the ink jet recording element is subject to hot, softnip calendering at a temperature of 65 ° C and a pressure of 14000 kg/m at a speed of from 0.15 m/s to 0.3 m/s.

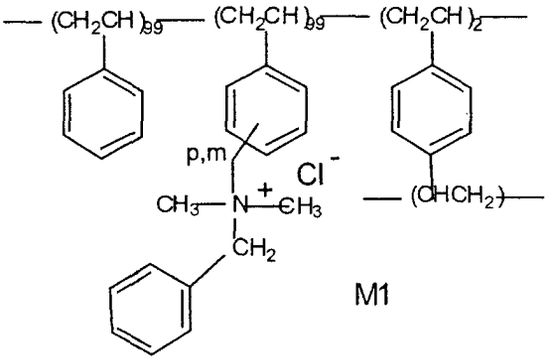
[0025] Ink jet inks used to image the recording elements of the present invention are well-known in the art. The ink compositions used in ink jet printing typically are liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, and the like. The solvent or carrier liquid can be solely water or can be water mixed with other water-miscible solvents such as polyhydric alcohols. Inks in which organic materials such as polyhydric alcohols are the predominant carrier or solvent liquid may also be used. Particularly useful are mixed solvents of water and polyhydric alcohols. The dyes used in such compositions are typically water-soluble direct or acid type dyes. Such liquid compositions have been described extensively in the prior art including, for example, U.S. Patents 4,381,946; 4,239,543 and 4,781,758.

[0026] The following examples further illustrate the invention.

Example 1 - Dye Light Stability

Control Element 1

[0027] Kodak Ektacolor Edge® F paper base, a pigmented, resin-coated paper support, was coated with an approximately 8 μm thick gelatin/mordant receiving layer consisting of 7.53 g/m^2 of gelatin, 1.08 g/m^2 of cationic mordant MI, shown below, 0.1 g/m^2 of spreading agent 10-G (Olin) and 0.026 g/m^2 of formaldehyde hardener. The receiving layer was coated from an aqueous solution at a 0.01 cm. wet laydown and dried at 50°C.



M1

Element 1 of the Invention

[0028] This element was prepared the same as Control Element 1 except that it contained stabilizer 1 (above) at a level of 0.38 g/m^2. Stabilizer 1 and the other stabilizers of this invention are water-soluble and may be simply added to the aqueous gelatin/mordant coating melt.

Element 2 of the Invention

[0029] This element was prepared the same as Control Element 1 except that it contained stabilizer 2 at a level of 0.43 g/m^2.

Element 3 of the Invention

[0030] This element was prepared the same as Control Element 1 except that it contained stabilizer 3 at a level of 0.45 g/m^2.

Element 4 of the Invention

[0031] This element was prepared the same as Control Element 1 except that it contained stabilizer 4 at a level of 0.49 g/m^2.

Printing

[0032] Images were printed using a Hewlett Packard Desk Jet ® 695C ink jet printer loaded with ink cartridges containing Reactive Red 31 (Lyson® magenta) or Direct Yellow 132 (Intrajet® yellow) aqueous soluble dyes . The inks were prepared at a concentration to yield an optical transmission density of 1.0 in a 1 cm cell at 1000-fold dilution. The aqueous-based inks also contained 6.0 weight percent glycerol, 6.0 weight percent diethylene glycol and 0.5 weight percent Surfynol® 465. The inks were printed in steps to yield various reflection densities, including a density of approximately 1.0.

Light Stability

[0033] Reflection densities of the various printed samples were measured with an X-Rite® 338 densitometer. Samples were then exposed for one week to simulated daylight having an intensity of 50 Klux. Reflection densities were then remeasured, and the percentage losses in density were determined. The following results were obtained:

Table I

Element	% Loss in Green Density of Reactive Red 31	% Loss in Blue Density of Direct Yellow 132
Control 1	35	22
1	15	6
2	14	6
3	16	4
4	17	5

[0034] The above results show that the elements of this invention provide substantial reductions in light-induced fade for both the magenta Reactive Red 31 and the yellow Direct Yellow 132 images compared to the control element without any stabilizer.

Image Quality

[0035] In a test of resistance to high-humidity induced image smear, samples of resolution charts were also printed on the control element and on the elements 1-4 above and then exposed for three days to 38°C/90% relative humidity. None of the elements showed significant image smearing in the high humidity keeping test.

Example 2 Dye Light Stability With Different Mordant

Control Element 2

[0036] Kodak Ektacolor Edge® F paper base, a pigmented, resin-coated paper support, was coated with an approximately 8 μm thick gelatin/mordant receiving layer consisting of 7.53 g/m^2 of gelatin, 1.08 g/m^2 of cationic mordant, poly(N,N-dimethyl-N-octadecyl-N-vinylbenzyl-ammonium chloride), poly(styrene-co-1-vinylimidazole-co-3-hydroxyethyl-1-vinylimidazolium chloride) (5:4:1 mole ratio), 0.1 g/m^2 of spreading agent 10-G (Olin) and 0.026 g/m^2 of formaldehyde hardener. The receiving layer was coated from an aqueous solution at a 0.01 cm wet laydown and dried at 50°C.

Element 5 of the Invention

[0037] This element was prepared the same as Control Element 2 except that it contained stabilizer 1 at a level of 0.38 g/m^2. Stabilizer 1 was simply added to the aqueous gelatin/mordant coating melt.

Printing

[0038] Images were printed as in Example 1.

Light Stability

[0039] Light stability measurements were carried out for Reactive Red 31 as in Example 1, and the results are given in Table II. The following results were obtained:

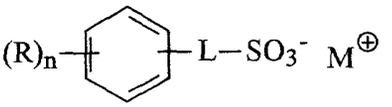
Table II

Element	% Loss in Green Density of Reactive Red 31
Control 2	17
5	12

[0040] The above results show that the element of the invention had good light stability compared to the control element.

Claims

1. An ink jet recording element comprising a substrate having thereon an image-receiving layer comprising a polymeric mordant and a polymeric binder containing a stabilizer having the following formula:



wherein:

each R individually represents a substituted or unsubstituted alkyl or alkoxy group having from 1 to 7 carbon atoms; a phenyl group having from 6 to 10 carbon atoms; a phenoxy group having from 6 to 10 carbon atoms; a carbonamido group having from 1 to 8 carbon atoms; or two or more R groups can be combined together to form a ring structure;
n is 1 to 4;
L is a linking group containing at least one carbon atom; and
M^+ is a monovalent cation;

with the proviso that the total number of carbon atoms in all the R's and L taken together is at least 3, and at least one R is said alkoxy group.

2. The recording element of Claim 1 wherein said mordant is a cationic polymer.

3. The recording element of Claim 2 wherein said mordant contains a quaternary amine group.

4. The recording element of Claim 1 wherein said mordant is protonated amine-containing polymer.

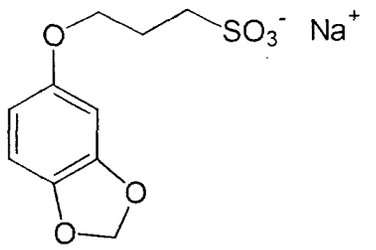
5. The recording element of Claim 1 wherein said polymeric binder is gelatin or poly(vinyl alcohol).

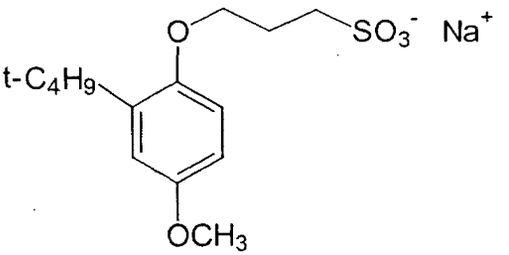
6. The recording element of Claim 1 wherein said L contains at least one methylene group.

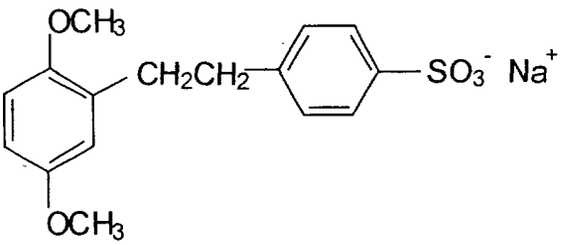
7. The recording element of Claim 1 wherein said M is Na, K or NH_4.

8. The recording element of Claim 1 wherein the stabilizer is present at an amount of from 0.04 to 1.6 g/m^2.

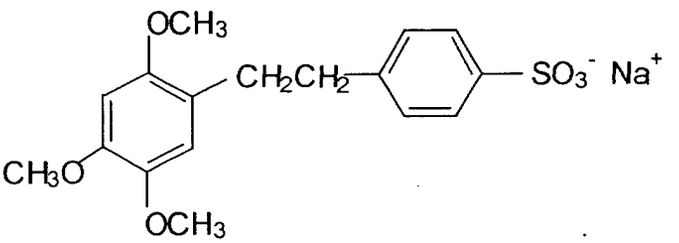
9. The recording element of Claim 1 wherein said stabilizer is







or



10. An ink jet printing method, comprising the steps of:

A) providing an ink jet printer that is responsive to digital data signals;
B) loading said printer with an ink jet recording element as described in claim 1;
C) loading said printer with an ink jet ink composition; and
D) printing on said ink jet recording element using said ink jet ink in response to said digital data signals.