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(72) Inventors:

- **Lingier, Stefaan
2640, Mortsel (BE)**
- **Loccufier, Johan
2640, Mortsel (BE)**

(71) Applicant: **AGFA-GEVAERT**

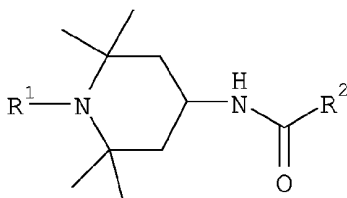
2640 Mortsel (BE)

(54) **Ink jet image improved for light-fastness**

(57) An ink jet recording material is disclosed comprising a support and a porous ink receiving layer comprising a binder, a pigment and a light-stabilizer according to following general formula (I) :

wherein R¹ and R² are defined in the description.

The finished ink jet color image shows a strong improvement in light-fastness.



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Description

FIELD OF THE INVENTION

- 5 **[0001]** The present invention relates to an ink jet recording material having an improved stabilization of the finished image against color fading due to light.

BACKGROUND OF THE INVENTION

- 10 **[0002]** In the majority of applications printing proceeds by pressure contact of an ink-loaden printing form with an ink-receiving material which is usually plain paper. The most frequently used impact printing technique is known as lithographic printing based on the selective acceptance of oleophilic ink on a suitable receptor. In recent times however so-called non-impact printing systems have replaced classical pressure-contact printing to some extent for specific applications. A survey is given e.g. in the book "Principles of Non Impact Printing" by Jerome L. Johnson (1986),
15 Palatino Press, Irvine, CA 92715, USA.

Among non-impact printing techniques ink jet printing has become a popular technique because of its simplicity, convenience and low cost. Especially in those instances where a limited edition of the printed matter is needed ink jet printing has become a technology of choice. A recent survey on progress and trends in ink jet printing technology is given by Hue P. Le in *Journal of Imaging Science and Technology* Vol. 42 (1), Jan/Febr 1998.

- 20 In ink jet printing tiny drops of ink fluid are projected directly onto an ink receptor surface without physical contact between the printing device and the receptor. The printing device stores the printing data electronically and controls a mechanism for ejecting the drops image-wise. Printing is accomplished by moving the print head across the paper or vice versa. Early patents on ink jet printers include US 3,739,393, US 3,805,273 and US 3,891,121.

- [0003]** The jetting of the ink droplets can be performed in several different ways. In a first type of process a continuous droplet stream is created by applying a pressure wave pattern. This process is known as continuous ink jet printing. In a first embodiment the droplet stream is divided into droplets that are electrostatically charged, deflected and recollected, and into droplets that remain uncharged, continue their way undeflected, and form the image. Alternatively, the charged deflected stream forms the image and the uncharged undeflected jet is recollected. In this variant of continuous ink jet printing several jets are deflected to a different degree and thus record the image (multideflection system). According to a second process the ink droplets can be created "on demand" ("DOD" or "drop on demand" method) whereby the printing device ejects the droplets only when they are used in imaging on a receiver thereby avoiding the complexity of drop charging, deflection hardware, and ink recollection. In drop-on-demand the ink droplet can be formed by means of a pressure wave created by a mechanical motion of a piezoelectric transducer (so-called "piezo method"), or by means of discrete thermal pushes (so-called "bubble jet" method, or "thermal jet" method).

- 35 Ink compositions for ink jet typically include following ingredients : dyes or pigments, water and/or organic solvents, humectants such as glycols, detergents, thickeners, polymeric binders, preservatives, etc.. It will be readily understood that the optimal composition of such an ink is dependent on the ink jetting method used and on the nature of the substrate to be printed. The ink compositions can be roughly divided in :

- 40 - water based ; the drying mechanism involves absorption, penetration and evaporation;
- oil based ; the drying involves absorption and penetration;
- solvent based ; the drying mechanism involves primarily evaporation;
- hot melt or phase change : the ink vehicle is liquid at the ejection temperature but solid at room temperature ; drying is replaced by solidification;
45 - UV-curable ; drying is replaced by polymerization.

[0004] It is known that the ink-receiving layers in ink-jet recording elements must meet different stringent requirements :

- 50 - The ink-receiving layer should have a high ink absorbing capacity, so that the dots will not flow out and will not be expanded more than is necessary to obtain a high optical density.
- The ink-receiving layer should have a high ink absorbing speed (short ink drying time) so that the ink droplets will not feather if smeared immediately after applying.
- The ink dots that are applied to the ink-receiving layer should be substantially round in shape and smooth at their peripheries. The dot diameter must be constant and accurately controlled.
55 - The receiving layer must be readily wetted so that there is no "puddling", i.e. coalescence of adjacent ink dots, and an earlier absorbed ink drop should not show any "bleeding", i.e. overlap with neighbouring or later placed dots.
- Transparent ink-jet recording elements must have a low haze-value and be excellent in transmittance properties.

- After being printed the image must have a good resistance regarding water-fastness, light-fastness, and good endurance under severe conditions of temperature and humidity.
- The ink jet recording element may not show any curl or sticky behaviour if stacked before or after being printed.
- The ink jet recording element must be able to move smoothly through different types of printers.

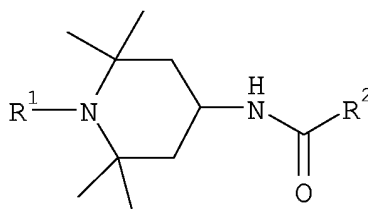
All these properties are often in a relation of trade-off. It is difficult to satisfy them all at the same time.

[0005] A particular problem is the stability of the color densities of the finished color ink jet image when exposed to light for a longer period ("light-fastness"). As well-known by those skilled in the art the light fading of colorants is mainly due to an oxidative decomposition of the colorant catalyzed by light, in particular by the UV spectral part. Therefore, there is a permanent need of more effective compounds which stabilize the colorants of the ink jet image against fading by light (in short, better "light-stabilizers" or better "antioxidants").

SUMMARY OF THE INVENTION

[0006] The present invention seeks to realize an improvement in light-fastness of the colorants of the finished image obtained by ink jet printing.

[0007] The above-mentioned advantageous property is realised by providing an ink jet recording material comprising a support and a porous ink receiving layer comprising a binder, a pigment and a compound according to following general formula (I) :



wherein R¹ represents a hydrogen atom, a hydroxyl group, an oxyradical group, an aliphatic group, an acyl group, an aliphatic oxy group or an acyloxy group; and R² represents an aliphatic group having at least three carbon atoms and at least two hydroxyl groups.

[0008] Further advantages and embodiments of the present invention will become apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The different layers and particular ingredients of the ink recording medium according to the present invention will now be explained in detail.

- the support

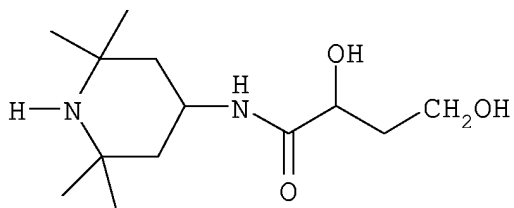
[0010] The support for use in the present invention can be chosen from paper type and polymeric type supports well-known from photographic technology. Paper types include plain paper, cast coated paper, polyethylene coated paper and polypropylene coated paper. Polymeric supports include cellulose acetate propionate or cellulose acetate butyrate, polyesters such as polyethylene terephthalate and polyethylene naphthalate, polyamides, polycarbonates, polyimides, polyolefins, poly(vinylacetals), polyethers and polysulfonamides. Other examples of useful high-quality polymeric supports for the present invention include opaque white polyesters and extrusion blends of polyethylene terephthalate and polypropylene. Polyester film supports and especially polyethylene terephthalate are preferred because of their excellent properties of dimensional stability. When such a polyester is used as the support material, a subbing layer may be employed to improve the bonding of the ink-receiving layer to the support. Useful subbing layers for this purpose are well known in the photographic art and include, for example, polymers of vinylidene chloride such as vinylidene chloride /acrylonitrile /acrylic acid terpolymers or vinylidene chloride /methyl acrylate /itaconic acid terpolymers.

- the ink receiving layer

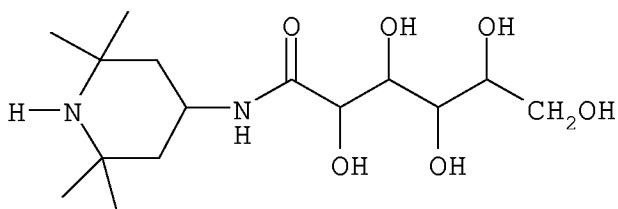
[0011] It is the gist of the present invention that the porous ink receiving layer contains, apart from a binder and a

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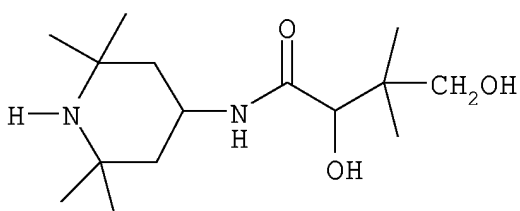
pigment, a light-stabilizer according to general formula (I) as shown above. The 4-acylamino-2,2,6,6-tetramethylpiperazine derivatives according to this general formula (I) are known from US 6,232,469. However, their particular advantage as light-stabilizers in a particular type of ink jet recording material was not recognized in the latter disclosure. Useful substances include following light-stabilizers (LS-1 to 13) without being limited thereto.



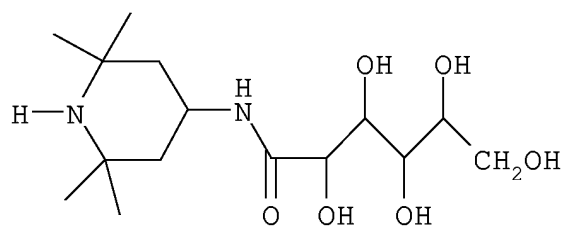
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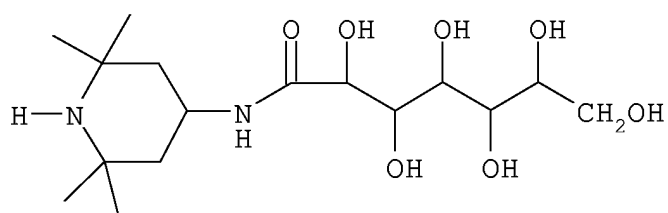
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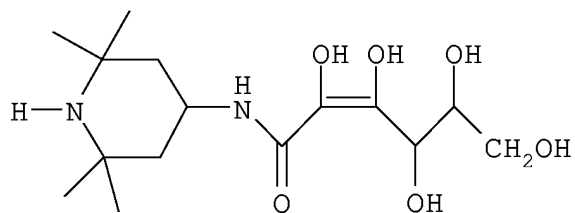
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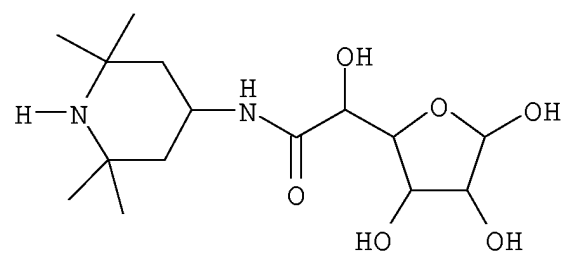
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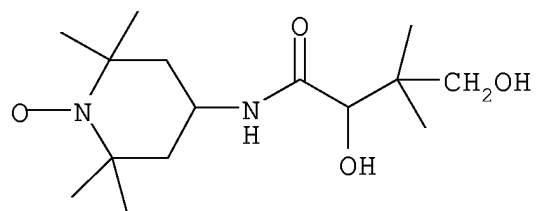
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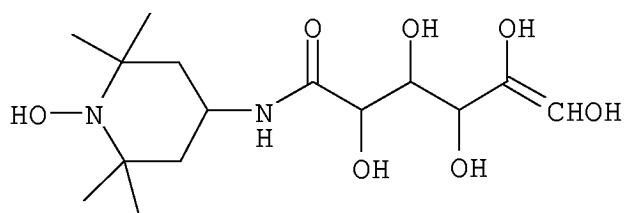
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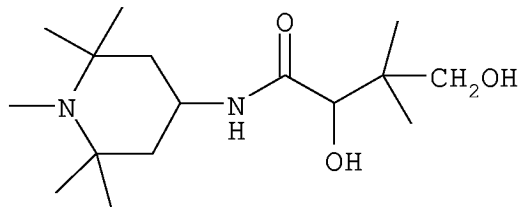
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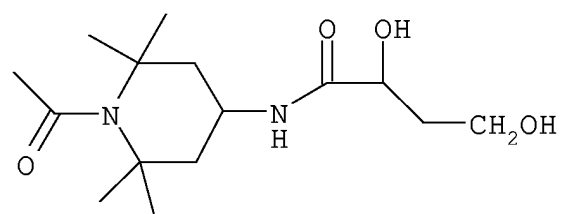
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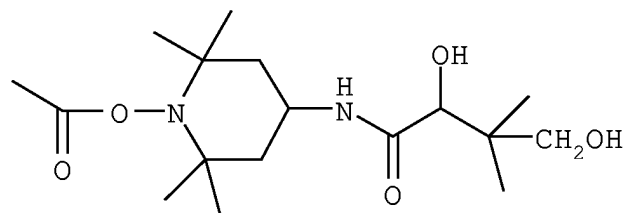
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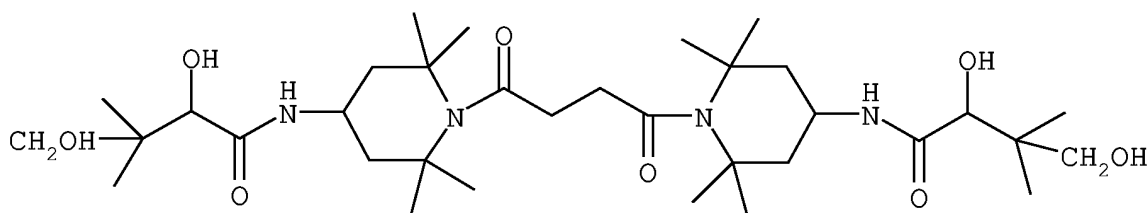
(LS-10)



(LS-11)



(LS-12)



(LS-13)

A preferred effective compound is light-stabilizer LS-4.

The light-stabilizers are preferably added to the coating solution of the ink receiving layer as aqueous solutions. The amount of the antioxidant in the layer (or in the coating composition ?) is preferably comprised between 0.5 and 3 g/m².

[0012] The binder can be chosen from a list of compounds well-known in the art including hydroxyethyl cellulose; hydroxypropyl cellulose; hydroxyethylmethyl cellulose; hydroxypropyl methyl cellulose; hydroxybutylmethyl cellulose; methyl cellulose; sodium carboxymethyl cellulose; sodium carboxymethylhydroxyethyl cellulose; water soluble ethylhydroxyethyl cellulose; cellulose sulfate; polyvinyl alcohol; vinylalcohol copolymers; polyvinyl acetate; polyvinyl acetal; polyvinyl pyrrolidone; polyacrylamide; acrylamide/acrylic acid copolymer; polystyrene, styrene copolymers; acrylic or methacrylic polymers; styrene/acrylic copolymers; ethylene-vinylacetate copolymer; vinylmethyl ether/maleic acid copolymer; poly(2-acrylamido-2-methyl propane sulfonic acid); poly(diethylene triamine-co-adipic acid); polyvinyl pyridine; polyvinyl imidazole; polyethylene imine epichlorohydrin modified; polyethylene imine ethoxylated; polyethylene oxide; polyurethane; melamine resins; gelatin; carrageenan; dextran; gum arabic; casein; pectin; albumin; starch; collagen derivatives; collodion and agar-agar.

A preferred binder for the practice of the present invention is a polyvinylalcohol (PVA), a vinylalcohol copolymer or modified polyvinyl alcohol. Most preferably, the polyvinyl alcohol is a cationic type polyvinyl alcohol, such as the cationic polyvinyl alcohol grades from Kuraray, such as POVAL C506, POVAL C118, and from Nippon Goshei.

[0013] Mixtures of two or more binders can be used.

[0014] The pigment used in the ink receiving layer is preferably an inorganic pigment, which can be chosen from neutral, anionic and cationic pigment types. Useful pigments include e.g. silica, talc, clay, hydrotalcite, kaolin, diatomaceous earth, calcium carbonate, magnesium carbonate, basic magnesium carbonate, aluminosilicate, aluminum trihydroxide, aluminum oxide (alumina), titanium oxide, zinc oxide, barium sulfate, calcium sulfate, zinc sulfide, satin white, alumina hydrate such as boehmite, zirconium oxide or mixed oxides.

Preferably, the pigment is a cationic type pigment selected from alumina hydrates, aluminum oxides, aluminum hydroxides, aluminum silicates, and cationically modified silicas.

A preferred type of alumina hydrate is crystalline boehmite, or γ -AlO(OH). Useful types of boehmite include, in powder form, DISPERAL, DISPERAL HP14 and DISPERAL 40 from Sasol, MARTOXIN VPP2000-2 and GL-3 from Martinswerk GmbH.; liquid boehmite alumina systems, e.g. DISPAL 23N4-20, DISPAL 14N-25, DISPERAL AL25 from Sasol. Patents on alumina hydrate include EP 500021, EP 634286, US 5,624,428, EP 742108, US 6,238,047, EP 622244, EP 810101, etc.. Useful cationic aluminum oxide (alumina) types include α -Al₂O₃ types, such as NORTON E700, available from Saint-Gobain Ceramics & Plastics, Inc, and γ -Al₂O₃ types, such as ALUMINUM OXID C from Degussa; other aluminum

oxide grades, such as BAIKALOX CR15 and CR30 from Baikowski Chemie; DURALOX grades and MEDIALOX grades from Baikowski Chemie, BAIKALOX CR80, CR140, CR125, B105CR from Baikowski Chemie; CAB-O-SPERSE PG003 trademark from Cabot, CATALOX GRADES and CATAPAL GRADES from Sasol, such as PLURALOX HP14/150; colloidal Al_2O_3 types, such as ALUMINASOL 100; ALUMINASOL 200, ALUMINASOL 220, ALUMINASOL 300, and ALUMINASOL 520 trademarks from Nissan Chemical Industries or NALCO 8676 trademark from ONDEO Nalco.

[0015] Other useful cationic inorganic pigments include aluminum trihydroxides such as Bayerite, or $\alpha\text{-Al}(\text{OH})_3$, such as PLURAL BT, available from Sasol, and Gibbsite, or $\gamma\text{-Al}(\text{OH})_3$, such as MARTINAL grades from Martinswerk GmbH, MARTIFIN grades, such as MARTIFIN OL104, MARTIFIN OL 107 and MARTIFIN OL111 from Martinswerk GmbH, MICRAL grades, such as MICRAL 1440, MICRAL 1500; MICRAL 632; MICRAL 855; MICRAL 916; MICRAL 932; MICRAL 932CM; MICRAL 9400 from JM Huber company; HIGILITE grades, e.g. HIGILITE H42 or HIGILITE H43M from Showa Denka K.K..

Another useful type of cationic pigment is zirconium oxide such as NALCO OOSS008 trademark of ONDEO Nalco, acetate stabilized ZrO_2 , ZR20/20, ZR50/20, ZR100/20 and ZRYS4 trademarks from Nyacol Nano Technologies.

Useful mixed oxides are SIRAL grades from Sasol, colloidal metal oxides from Nalco such as Nalco 1056, Nalco TX10496, Nalco TX11678. Another preferred type of inorganic pigment is silica which can be used as such in its anionic form or after cationic modification. Silica as pigment in ink receiving elements is disclosed in numerous old and recent patents, e.g. US 4,892,591, US 4,902,568, EP 373573, EP 423829, EP 487350, EP 493100, EP 514633, etc.. The silica can be chosen from different types, such as crystalline silica, amorphous silica, precipitated silica, fumed silica, silica gel, spherical and non-spherical silica. The silica may contain minor amounts of metal oxides from the group Al, Zr, Ti. Useful types include AEROSIL OX50 (BET surface area $50 \pm 15 \text{ m}^2/\text{g}$, average primary particle size 40 nm, SiO_2 content $> 99.8\%$, Al_2O_3 content $< 0.08\%$), AEROSIL MOX170 (BET surface area $170 \text{ g}/\text{m}^2$, average primary particle size 15 nm, SiO_2 content $> 98.3\%$, Al_2O_3 content 0.3-1.3%), AEROSIL MOX80 (BET surface area $80 \pm 20 \text{ g}/\text{m}^2$, average primary particle size 30 nm, SiO_2 content $> 98.3\%$, Al_2O_3 content 0.3-1.3%), or other hydrophilic AEROSIL grades available from Degussa-Hüls AG, which may give aqueous dispersions with a small average particle size ($< 500 \text{ nm}$).

[0016] Cationically modified silica can be prepared by following methods, without meaning to be limitative :

(1) subjecting silica to a surface treatment with an inorganic cationic compound such as particular metal oxides and oxyhydroxides, e.g. aluminum oxides, and alumina hydrates such as boehmite and pseudo-boehmite; a useful cationic inorganic compound to modify silica is pseudo-boehmite. Pseudo-boehmite is also called boehmite gel and is fine particulate alumina hydrate having a needle form. The composition thereof is generally represented by $\text{Al}_2\text{O}_3 \cdot 1.5\text{-}2 \text{ H}_2\text{O}$ and differs from that of crystalline boehmite;

(2) by subjecting silica to a surface treatment with an organic compound having both an amino group or quaternary ammonium group thereof or a quaternary phosphonium group, and a functional group having reactivity to a silanol group on the surface of silica, such as aminoalkoxysilane or aminoalkyl glycidyl ether or isopropanol amine;

(3) by polymerisation of a cationic or amino functional monomer in the presence of a silica.

[0017] In an alternative embodiment the pigment may be chosen from organic particles such as polystyrene, polymethyl methacrylate, silicones, melamine-formaldehyde condensation polymers, urea-formaldehyde condensation polymers, polyesters and polyamides. Mixtures of inorganic and organic pigments can be used. However, most preferably the pigment is an inorganic pigment.

The pigment must be present in a sufficient coverage in order to render the ink receiving layer sufficiently porous.

For obtaining glossy ink receiving layers the particle size of the pigment should preferably be smaller than 500 nm. In order to obtain a porous glossy layer which can serve as an ink receiving layer for fast ink uptake the pigment/binder ratio should be at least 4. Only at these high ratios the binder is no longer able to fill up all pores and voids created by the pigments in the coating. To achieve a sufficient porosity of the coating for fast ink uptake the pore volume of these highly pigmented coatings should be higher than 0.1 ml/g of coated solids. This pore volume can be measured by gas adsorption (nitrogen) or by mercury diffusion.

[0018] Apart from the essential ingredients described above a cationic substance acting as mordant may be present in the ink receiving layer. Such substances increase the capacity of the layer for fixing and holding the dye of the ink droplets. A particularly suited compound is a poly(diallyldimethylammonium chloride) or, in short, a poly(DADMAC). These compounds are commercially available from several companies, e.g. Aldrich, Nalco, CIBA, Nitto Boseki Co., Clariant, BASF and EKA Chemicals.

Other useful cationic compounds include DADMAC copolymers such as copolymers with acrylamide, e.g. NALCO 1470 trade mark of ONDEO Nalco or PAS-J-81, trademark of Nitto Boseki Co., such as copolymers of DADMAC with acrylates, such as Nalco 8190, trademark of ONDEO Nalco; copolymers of DADMAC with SO_2 , such as PAS-A-1 or PAS-92, trademarks of Nitto Boseki Co., copolymer of DADMAC with maleic acid, e.g. PAS-410, trademark of Nitto Boseki Co., copolymer of DADMAC with diallyl(3-chloro-2-hydroxypropyl)amine hydrochloride, eg. PAS-880, trademark of

Nitto Boseki Co., dimethylamine-epichlorohydrine copolymers, e.g. Nalco 7135, trademark of ONDEO Nalco or POLY-FIX 700, trade name of Showa High Polymer Co.; other POLYFIX grades which could be used are POLYFIX 601, POLYFIX 301, POLYFIX 301A, POLYFIX 250WS, and POLYFIX 3000; NEOFIX E-117, trade name of Nicca Chemical Co., a polyoxyalkylene polyamine dicyanodiamine, and REDIFLOC 4150, trade name of EKA Chemicals, a polyamine; MADAME (methacrylatedimethylaminoethyl = dimethylaminoethyl methacrylate) or MADQUAT (methacryloxyethyltrimethylammonium chloride) modified polymers, e.g. ROHAGIT KL280, ROHAGIT 210, ROHAGIT SL144, PLEX 4739L, PLEX 3073 from Röhm, DIAFLOC KP155 and other DIAFLOC products from Diafloc Co., and BMB 1305 and other BMB products from EKA chemicals; cationic epichlorohydrin adducts such as POLYCUP 171 and POLYCUP 172, trade names from Hercules Co.; from Cytec industries: CYPRO products, e.g. CYPRO 514/515/516, SUPERFLOC 507/521/567; cationic acrylic polymers, such as ALCOSTAT 567, trademark of CIBA, cationic cellulose derivatives such as CELQUAT L-200, H-100, SC-240C, SC-230M, trade names of Starch & Chemical Co., and QUATRISOFT LM200, UCARE polymers JR125, JR400, LR400, JR30M, LR30M and UCARE polymer LK; fixing agents from Chukyo Europe: PALSET JK-512, PALSET JK512L, PALSET JK-182, PALSET JK-220, WSC-173, WSC-173L, PALSET JK-320, PALSET JK-320L and PALSET JK-350; polyethyleneimine and copolymers, e.g. LUPASOL, trade name of BASF AG; triethanolaminetitanium-chelate, e.g. TYZOR, trade name of Du Pont Co.; copolymers of vinylpyrrolidone such as VIVIPRINT 111, trade name of ISP, a methacrylamido propyl dimethylamine copolymer; with dimethylaminoethylmethacrylate such as COPOLYMER 845 and COPOLYMER 937, trade names of ISP; with vinylimidazole, e.g. LUVIQUAT CARE, LUVITEC 73W, LUVITEC VPI55 K18P, LUVITEC VP155 K72W, LUVIQUAT FC905, LUVIQUAT FC550, LUVIQUAT HM522, and SOKALAN HP56, all trade names of BASF AG; polyamidoamines, e.g. RETAMINOL and NADAVIN, trade marks of Bayer AG; phosphonium compounds such as disclosed in EP 609930 and other cationic polymers such as NEOFIX RD-5, trademark of Nicca Chemical Co.

[0019] The ink receiving layer, and an optional auxiliary layer, such as a backing layer for anti-curl purposes, may further contain well-known conventional ingredients, such as surfactants serving as coating aids, hardening agents, plasticizers, whitening agents and matting agents.

Surfactants may be incorporated in the layers of the recording element of the present invention. They can be any of the cationic, anionic, amphoteric, and non-ionic ones as described in JP-A 62-280068 (1987). Examples of the surfactants are N-alkylamino acid salts, alkylether carboxylic acid salts, acylated peptides, alkylsulfonic acid salts, alkylbenzene and alkyl-naphthalene sulfonic acid salts, sulfosuccinic acid salts, α -olefin sulfonic acid salts, N-acylsulfonic acid salts, sulfonated oils, alkylsulfonic acid salts, alkylether sulfonic acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers, alkylallylformaldehyde condensed acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers, alkylallylformaldehyde condensed polyoxyethylene ethers, blocked polymers having polyoxypropylene, polyoxyethylene polyoxypropylalkylethers, polyoxyethyleneether of glycolestes, polyoxyethyleneether of sorbitanesters, polyoxyethyleneether of sorbitolesters, polyethyleneglycol aliphatic acid esters, glycerol esters, sorbitane esters, propyleneglycol esters, sugaresters, fluoro C_2 - C_{10} alkylcarboxylic acids, disodium N-perfluorooctanesulfonyl glutamate, sodium 3-(fluoro- C_6 - C_{11} -alkyloxy)-1- C_3 - C_4 alkyl sulfonates, sodium 3-(ω -fluoro- C_6 - C_8 -alkanoyl-N-ethylamino)-1-propane sulfonates, N-[3-(perfluorooctanesulfonamide)-propyl]-N,N-dimethyl-N-carboxymethylene ammonium betaine, fluoro- C_{11} - C_{20} alkylcarboxylic acids, perfluoro- C_7 - C_{13} -alkyl-carboxylic acids, perfluorooctane sulfonic acid diethanolamide, Li, K and Na perfluoro- C_4 - C_{12} -alkyl sulfonates, N-propyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide, perfluoro- C_6 - C_{10} -alkylsulfonamide-propyl-sulfonyl-glycinates, bis-(N-perfluorooctylsulfonyl-N-ethanolaminoethyl)phosphonate, mono-perfluoro C_6 - C_{16} alkyl-ethyl phosphonates, and perfluoroalkylbetaine.

Useful cationic surfactants include N-alkyl dimethyl ammonium chloride, palmityl trimethyl ammonium chloride, dodecyltrimethylamine, tetradecyltrimethylamine, ethoxylated alkyl guanidine-amine complex, oleamine hydroxypropyl bistrimonium chloride, oleyl imidazoline, stearyl imidazoline, cocamine acetate, palmitamine, dihydroxyethylcocamine, cocotrimonium chloride, alkyl polyglycoether ammonium sulphate, ethoxylated oleamine, lauryl pyridinium chloride, N-oleyl-1,3-diaminopropane, stearamidopropyl dimethylamine lactate, coconut fatty amide, oleyl hydroxyethyl imidazoline, isostearyl ethylimidonium ethosulphate, lauramidopropyl PEG-dimoniumchloride phosphate, palmityl trimethylammonium chloride, and cetyltrimethylammonium bromide.

Especially useful are the fluorocarbon surfactants as described in e.g. US-P 4,781,985, having a structure of: $F(CF_2)_{4-9}CH_2CH_2SCH_2CH_2N^+R_3X^-$ wherein R is a hydrogen or an alkyl group; and in US-P 5,084,340, having a structure of:

$CF_3(CF_2)_mCH_2CH_2O(CH_2CH_2O)_nR$ wherein $m = 2$ to 10 ; $n = 1$ to 18 ; R is hydrogen or an alkyl group of 1 to 10 carbon atoms. These surfactants are commercially available from DuPont and 3M. The concentration of the surfactant component in the ink-receiving layer is typically in the range of 0.1 to 2 %, preferably in the range of 0.4 to 1.5 % and is most preferably 0.75 % by weight based on the total dry weight of the layer.

[0020] The ink-receiving layer and the optional auxiliary layer(s) may be crosslinked to provide such desired features

as waterfastness and non-blocking characteristics. The crosslinking is also useful in providing abrasion resistance and resistance to the formation of fingerprints on the element as a result of handling. There are a vast number of known crosslinking agents - also known as hardening agents - that will function to crosslink film forming binders. Hardening agents can be used individually or in combination and in free or in blocked form. A great many hardeners, useful for the present invention, are known, including formaldehyde and free dialdehydes, such as succinaldehyde and glutaraldehyde, blocked dialdehydes, active esters, sulfonate esters, active halogen compounds, isocyanate or blocked isocyanates, polyfunctional isocyanates, melamine derivatives, s-triazines and diazines, epoxides, active olefins having two or more active bonds, carbodiimides, zirconium complexes, e.g. BACOTE 20, ZIRMEL 1000 or zirconium acetate, trademarks of MEL Chemicals, titanium complexes, such as TYZOR grades from DuPont, isoxazolium salts substituted in the 3-position, esters of 2-alkoxy-N-carboxy-dihydroquinoline, N-carbamoylpyridinium salts, hardeners of mixed function, such as halogen-substituted aldehyde acids (e.g. mucochloric and mucobromic acids), onium substituted acroleins and vinyl sulfones and polymeric hardeners, such as dialdehyde starches and copoly(acroleinmethacrylic acid), and oxazoline functional polymers, e.g. EPOCROS WS-500, and EPOCROS K-1000 series, and maleic anhydride copolymers, e.g. GANTREZ AN119

In the practice of this invention boric acid is a preferred crosslinker.

The ink-receiving layer and the optional auxiliary layer(s) may also comprise a plasticizer such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, glycerol monomethylether, glycerol monochlorohydrin, ethylene carbonate, propylene carbonate, urea phosphate, triphenylphosphate, glycerolmonostearate, propylene glycol monostearate, tetramethylene sulfone, n-methyl-2-pyrrolidone, n-vinyl-2-pyrrolidone.

[0021] The different layers can be coated onto support by any conventional coating technique, such as dip coating, knife coating, extrusion coating, spin coating, slide hopper coating and curtain coating.

[0022] The present invention will now be illustrated by the following examples without however being limited thereto.

EXAMPLES

Example 1

Preparation of the coating solution

[0023] To apply the light-stabilizing agent to ink jet print media, a coating liquid was prepared by adding 25 parts by solid weight of a 10% aqueous solution of the light-stabilizing compound LS-4 to 170 parts of water.

Coating and evaluation of the coated samples

[0024] The coating solution was applied to several different print media. Two different glossy porous media (A= Agfajet Universal Instant Dry Photograde Paper Glossy and B is the same, however without whitening agent) and two different non-porous media (C= Agfa Inkjet Photo Paper 2 in 1, and D= Agfajet Universal Photograde Paper dye glossy) were used as the basecoat. In order to change the concentration of the light-stabilizing additive, the thickness of the applied coating solution was varied. The application was performed by means of a doctor blade coater. The comparative samples were obtained by simply applying the aqueous solution to the recording media without the stabilizing agent. After the media were allowed to dry at room temperature for 24 hours, color patches with 50% and 100% ink of cyan, magenta, yellow and black were printed by means of a printer HP970Cxi (trademark of Hewlett-Packard). The light-fastness was evaluated by measuring the relative optical density loss of the printed samples after being exposed to light in a fade-o-meter, XENOTEST 150 (trademark: Original Hanau) with 180 kLux during 16 hours. The results are summarised in table 1.

TABLE 1 :

comparison of optical density loss of printed media treated with light-stabilizing additive:				
Color	Media	Relative optical density loss (%)		
		Without LS-4	With 0.25 g/m ² of LS-4	with 0.5 g/m ² of LS-4
Yellow	A	11	10	10
Yellow	B	19	11	10
Yellow	C	8	6	5
Yellow	D	7	5	7

TABLE 1 : (continued)

comparison of optical density loss of printed media treated with light-stabilizing additive:				
Color	Media	Relative optical density loss (%)		
		Without LS-4	With 0.25 g/m ² of LS-4	with 0.5 g/m ² of LS-4
Magenta	A	34	16	14
Magenta	B	30	19	19
Magenta	C	9	7	7
Magenta	D	14	14	14
Cyan	A	30	19	20
Cyan	B	25	21	21
Cyan	C	9	8	6
Cyan	D	13	8	10
Black	A	25	11	11
Black	B	22	12	10
Black	C	6	5	4
Black	D	7	6	5

[0025] As can be seen from the table, the porous materials (A and B) impregnated with stabiliser LS-4 show, especially for the magenta and the cyan ink, an important improvement in light-fastness.

Example 2

[0026] Two ink jet recording media (inv. and comp.) were prepared by coating on a resin-coated paper an ink receiving layer which composition is shown in table 2. The invention sample contained LS-4, the comparative sample not. The coating weight of the inorganic pigment was 28.2 g/m². Due to the high inorganic pigment / binder ratio, the ink receiving layers showed a porosity of 0.50 cc/g (measured by means of nitrogen adsorption).

TABLE 2

Compositions	
Alumina (Cab-o-Sperse PG003: 40%, supplied by Cabot Corp.)	704.3 g
Polyvinyl alcohol (Gohsefimer K210, supplied by Nippon Gohsei)	18.3 g
Boric acid	1.8 g
Comp. Sample: deionised water	477.5 g
Inv. Sample : 10 % sol. of LS-4	100 g
Deionized water	377.5 g

[0027] Color patches with 50% and 100% ink of cyan, magenta, yellow and black were printed on both samples by means of a wide format printer HP2500 (trademark Hewlett-Packard). The light-fastness was evaluated by measuring the relative optical density loss of the printed samples after being exposed to light in a fade-o-meter, XENOTEST 150 (trademark of Original Hanau) with 180 kLux during 16 hours.

The relative loss (%) in density of the four 50% color patches together, due to the light fading are shown in table 3.

TABLE 3

	Comp. sample Porous	Inv. sample Porous
Density loss (%)	47.9	31.4

[0028] As can be seen, the color stability was much improved when compound LS-4 was introduced in the porous

ink receiving layer.

Example 3

[0029] This example compares non-porous media (not according to the invention) with and without light-stabilizer in the ink receiving layer.

Two ink jet recording medium were prepared by coating on a resin-coated paper an ink absorbing layer which composition is shown in table 4 (with and without LS-4). The coating weight of the inorganic pigment was 20.0 g/m². Due to the fact that the pigment / binder ratio was much lower than in the previous example, these ink receiving layers showed no measurable porosity.

TABLE 4

Compositions	
Alumina (Cab-o-Sperse PG003: 40%, supplied by Cabot Corp.)	500.0 g
Polyvinyl alcohol (Gohsefimer K210, supplied by Nippon Gohsei)	100.0 g
Boric acid	10 g
Sample 1 : deionised water	1319 g
Sample 2 : 10 % sol. of LS-4	100 g
Deionized water	1219 g

[0030] The samples were printed and evaluated in the same way as described in previous example 2. The total relative loss (%) in density of the four 50% color patches together, due to the light fading are shown in table 5.

TABLE 5

	Sample 1 Non-porous	Sample 2 Non-porous
Density loss(%)	20.15	25.2

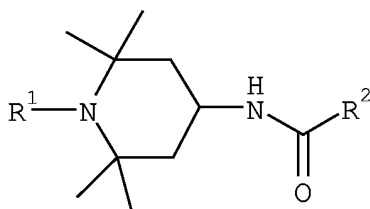
[0031] As can be seen from table 5, the introduction of the compound LS-4 in a material which does not show any porosity, does not improve the stability of the printed colors.

So this example proves that the advantageous effect in light-fastness is only seen in porous pigmented media according to the invention and not in non-porous ink jet media.

[0032] Having described in detail preferred embodiments of the current invention, it will now be apparent to those skilled in the art that numerous modifications can be made therein without departing from the scope of the invention as defined in the appending claims.

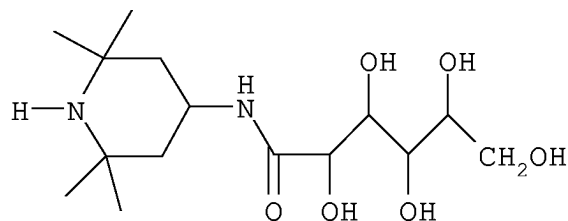
Claims

1. An ink jet recording material comprising a support and a porous ink receiving layer comprising a binder, a pigment and a compound according to following general formula (I) :



wherein R¹ represents a hydrogen atom, a hydroxyl group, an oxyradical group, an aliphatic group, an acyl group, an aliphatic oxy group or an acyloxy group; and R² represents an aliphatic group having at least three carbon atoms and at least two hydroxyl groups.

2. An ink jet recording material according to claim 1 wherein said compound according to general formula (I) is :



3. An ink jet recording material according to claim 1 or 2 wherein said pigment is an inorganic pigment.
4. An ink jet recording element according to claim 3 wherein said inorganic pigment is chosen from the group consisting of silica, alumina, alumina hydrate, aluminum silicate and aluminum trihydroxide.
5. An ink jet recording element according to any of claims 1 to 4 wherein said binder is a polyvinyl alcohol.
6. An ink jet recording element according to any of claims 1 to 5 wherein the amount pigment / amount binder ratio is at least 4.
7. An ink jet recording element according to any of claims 1 to 6 wherein the pore volume of the ink receiving layer is higher than 0.1 ml/g of coated solids, as measured by the nitrogen adsorption method.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 02 10 0755

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EPO FORM 1503 (03.82 (P04C01))

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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