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(54) Recording medium

(57) The present invention relates to a recording medium, in particular to a recording medium on which a variety of inks can be printed, which medium has quick ink absorption, good water fastness, high gloss, good light fastness and good ozone fastness.

A recording medium according to the invention comprises a support and a receiving layer adhered to this support, in which said receiving layer comprises at least one porous layer comprising at least one organic polymer, which receiving layer comprises a bottom layer and a top layer further away from the support than said bottom layer, wherein the average pore size in the bottom layer is larger than the average pore size in the top layer.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a recording medium, in particular to a recording medium on which a variety of inks can be printed which medium has quick ink absorption, good water fastness, high gloss, good light fastness and good ozone fastness.

BACKGROUND OF THE INVENTION

[0002] Recently, due to rapid industrial developments amongst others in the information technology, various methods and devices have been developed and brought into practical use in order to deliver printed hard copies.

[0003] Among these methods, ink jet printing has increasingly been employed not only in offices but also in homes because various materials can be printed at relatively low costs where compact hardware can be used and stable operation is obtained.

[0004] Because of the improved resolution of an ink jet printer, it becomes possible to produce a high quality photo-like print, and this again triggered the development of various printing sheets for the ink jet printing.

[0005] In general, the characteristics, essential for such a printing sheet are (1) a rapid drying property (a high ink absorbing rate), (2) an appropriate and uniform ink dot size (absence of oozing out), (3) good graininess after printing, (4) a highly true circle of a dot, (5) a highly intense color, (6) a high chroma (without darkening), (7) satisfactory water-proof, light resistance and ozone resistance of a printed part, (8) a high whiteness of a printing sheet, (9) a satisfactory storage performance of a printing sheet (without undergoing any yellowing after a prolonged storage period and without undergoing any oozing after a prolonged storage (satisfactory resistance to retarded oozing out), (10) a less deformable and satisfactorily stable size (sufficiently low curling behavior), (11) a satisfactory running over a hardware and the like.

[0006] In addition to the characteristics listed above, the printing sheet should have a high gloss, a high surface smoothness and a photographic paper-like appearance in order to obtain photo-like printed images using ink jet printing.

[0007] In general a printing sheet comprises a support and a receiving layer. One of the important properties of the receiving layer is the liquid absorption speed. The majority, if not all, of the ink solvent has to be absorbed by the layer itself. Only when paper or cloth or cellulose is used as a support, some part of the solvent may be absorbed by the support. It thus follows that when the ink-receiving layer comprises a binder and a filler they both should have a significant ability to absorb the ink solvent.

[0008] There are in general two approaches for producing ink-jet recording media with photographic quality and good drying properties.

[0009] One type of ink-jet recording media of photographic quality having reasonable drying properties is the so called "non-microporous film type", also known as "swellable type", as proposed in several patent publications such as JP-A-22 76 670. For this type of ink-jet recording medium, at least one ink receptive layer is coated on a support such as a paper or a transparent film. One way to improve the liquid absorption and drying rates of these media is the use of water swellable polymers. DE-A-223 48 23, DE-A-19721238 and US-A-4 379 804 disclose methods in which gelatin is used in ink- receptive layers of ink-jet receiving sheets. From these documents, it has become clear that gelatin has an advantageous function for the absorption of ink solvents. The gelatin is said to improve smudge resistance and to increase the image definition quality.

[0010] Also JP02-001359, JP2003-260867 and JP2003-320751 disclose IRL comprising water soluble polymers.

[0011] An other type of ink jet recording media is the microporous type, in which a microporous receiving layer is used. One way of obtaining a microporousn layer is the use of inorganic porous particles such as silica, alumina hydrate and pseudo-boehmite that are responsible for the porous character of the medium as described in e.g. EP-A-0 761 459 and EP-A-1 306 395 Also JP10-119423 and JP10-217601 disclose IRL comprising inorganic pigment particles and water-soluble binder to create high porosity. These media show good drying properties but their dye stability is not so good.

[0012] Another known approach is to provide a support with a microporous film, which can act as the ink receptive layer. However, this known technique may give problems as to the gloss of the media and may result in a low optical density of the printed images.

[0013] US- A-5 605 750 proposes an ink jet medium comprising a support, a thin microporous film as produced, among others, by the method mentioned in US-A-4 833 172 and an upper image-forming layer of porous pseudo-boehmite having an average pore radius of from 1 to 8 nm (10Å to 80Å). Said medium provides high optical density and good color gamut on the recorded images.

[0014] US -A-4 833 172 describes a method to produce a microporous film by stretching a sheet that comprises polyolefin, water insoluble siliceous particles and specific processing plasticisers, followed by removing said plasticiser after stretching. In order to increase the gloss, said microporous film may be calendered.

[0015] There are several other documents describing the use of a stretched microporous film for ink jet media such as WO-A-99/41086, US-A-4 861 644, WO-A-97/33758 and WO-A-02/053391.

[0016] Several patent publications e.g. EP-A-0 156 532 and US-A-2001/0021439, disclose a single porous layer of homogeneous structure while in other applications methods are disclosed for the design of an inkjet image recording material with two distinctive layers adjacent to each other, one with microporous characteristics and one with swellable characteristics. EP-A-1 211 089 and EP-A-1 176 029 disclose a two layer ink jet image receiving element wherein the layer adjacent to the support consists of a hydrophilic, fluid-absorbing swellable polymer and the outermost layer is an ink receptive layer comprising an open pore structure.

[0017] EP-A-0 812 697 discloses a two layer ink jet receiving element wherein the microporous layer is in-between the support and the ink receptive layer and US-A-6 132 858 disclose IRL comprising a microporous polymer structure by a phase inversion technology.

[0018] When comparing both solutions for providing an ink-jet recording medium (*viz*. a medium having a microporous layer or a medium having a water swellable layer), it was found that both solutions have their positive and negative characteristics.

[0019] On the one hand, the microporous ink-jet recording media have excellent drying properties, but generally suffer from dye fading. On the other hand the swellable type of ink-jet recording media may give less dye fading, but generally dry more slowly.

[0020] The multilayer materials with both a swellable layer and a distinctive microporous layer suffer basically from the same quality problems, as an outer microporous layer results in a bad dye fading behavior and a bad gloss, and an outer swellable layer with a microporous sublayer does not solve the drying problem.

[0021] There remains a strong need for ink-jet recording media having excellent drying properties and which show minimal dye fading. In addition, these ink-jet recording media should preferably have properties such as suitable durability, good sheet feeding property in ink-jet printers, good image density, as well as a good resolution and good gloss.

[0022] It is towards fulfilling this need that the present invention is directed.

SUMMARY OF THE INVENTION

[0023] It is an object of this invention to provide a recording medium for ink printing applications giving a quick ink absorption excellent drying characteristics and also excellent dye fading resistance under various circumstances in combination with a high gloss.

[0024] It has been found that these objectives can be met by providing a recording medium comprising a support and a receiving layer adhered to said support in which said receiving layer comprising at least one asymmetric porous layer comprising at least one organic polymer. An "asymmetric porous layer" is understood herein to be a layer that may be of a single (chemical) composition, but having a gradient in the average pore size in the direction perpendicular to the layer's surface. The asymmetric layer thus comprises zones of different porosities, but may nevertheless have been applied to the support in a single coating step (although this is not necessary). The asymmetric porous layer may be defined as comprising at least a top layer and a bottom layer. Preferably the thickness of the top layer is at most 2 μm. Preferably the average pore size in the top layer is from 0.001 μm to 1 μm. Preferably the average pore size in the bottom layer is larger than the average pore size in the top layer.

[0025] Thus the present invention provides a recording medium comprising a support and a receiving layer adhered to said support, wherein said receiving layer comprising at leas one porous layer having an asymmetric membrane structure, *viz.* the porous layer comprises a dense microporous top layer adjacent to a microporous bottom layer, which porous layer comprises at least one water-non soluble polymer. "Dense toplayer" means that the porosity of the toplayer is less than the porosity of the microporous bottom layer.

[0026] Pore diameters and pore volume as expressed herein, are suitably assessed by measuring the dimensions of the pores from the cross section pictures made by Scanning Electron Microscopy (SEM), which pictures are taken at a proper magnification. An average diameter is obtained by measuring a number of different cross sections, typically five different cross sections.

[0027] The term "water-non soluble polymer" as used herein, refers to a polymer (non microporous) that will not dissolve when contacted with water. Said polymer however are able to absorb water in an amount, typically ranging from 0.5 % to 20%.

[0028] The invention is furthermore directed to the method of ink jet recording and to the ink which gives the best results with the inventive recording medium of this invention.

DETAILED DESCRIPTION

[0029] The present invention is directed to a recording medium comprising a support and a receiving layer adhered to said support, in which said receiving layer comprises at least one microporous layer, which is preferably most remote from the support, meaning that the recording is directly done on the microporous layer. The advantage of the present invention results from the structure of the microporous layer and the polymer material forming the microporous structure. The microporous layer according to this invention preferably comprises at least a water non-soluble polymer. By using the water non soluble polymers the water fastness is improved considerably when compared to prior art products. This water non-soluble polymer should however not be water repellant, but it should be a hydrophilic polymer or a polymer which is made hydrophilic by suitable modification. Also water soluble polymers can be used, which have been made water insoluble, for example by cross-linking. The microporous layer of this invention is preferably asymmetric having a dense top layer and at least a less dense bottom layer. Optionally a middle section or middle layer can be distinguished. Another layer, or other layers might be present between the porous layer and the support. Such a layer, which is not microporous might be an adhesive layer or a layer, which improves the ink receiving properties or in general the physical property of the recording medium. The ink is preferably directly printed on the dense top layer providing the very good printing characteristics as mentioned before. The recording media of the present invention has advantages with regard to the drying speed, gloss and in general to the quality of the printed image thereon. Without wishing to be bound by theory, it is believed that when an image is printed on the inventive microporous media, the ink solvent is readily absorbed by said media through two mechanisms, *i.e.* through the ability of the layer to absorb water and through the capillary forces. This results in a dry surface in a short time. Due to this quick absorption, the resolution of image will not degrade and smearing or smudging of the image can be prevented. Also coalescence of ink drops which causes the "beading" phenomena can be avoided. By providing an asymmetric structure of the porous layer, having a dense top layer, the gloss can be maintained on an acceptable level.

[0030] The medium of this invention can be used in various printing applications such as inkjet, color copy, laser printing, screen printing, dye sublimation, flexography, and so on.

[0031] The ink to be used for printing on the media of the present invention can be chosen from a variety various of inks, such as liquid ink such as a aqueous inks (employing a dye or a pigment as a colorant), or oily inks, but also solid inks which are solid at an ambient temperature but melt and become liquid upon printing.

[0032] The water non soluble polymers of this invention can be selected from non water soluble polymers like cellulose, cellulose acetate, cellulose nitrate, polysulfone, ployethersulfone, polyamide, nylon, polyacrylate, polyesther, PVDF, polycarbonate, polyurethane, polyacrylonitrile, PVC, or polymers which are treated in order to be water non soluble. Treatment in this respect is done generally by cross-linking. Suitable examples of this kind of polymers can be selected from, but are not limited to: gelatine, gelatine derivatives, PVA, PVA derivatives and mixtures of these polymers.

[0033] Preferably the water non soluble polymers of this invention comprise at least one nitrogen atom in the molecular structure. Examples for the water non soluble nitrogen containing polymers are polyamide, polyurethane, polyacrylonitrile and so on and examples for the water soluble polymers which are treated to be water non soluble are gelatine and gelatine derivatives.

[0034] In the ink jet printing method, the ink droplets, or recording liquid, generally comprises a recording agent, such as a dye, and a relatively large amount of solvent in order to prevent clogging of the nozzle. The solvent, or carrier liquid, typically is made up of water, and organic material such as monohydric alcohols and the like. An image recorded as liquid droplets requires a receptor on which the recording liquid dries quickly without spreading. In order to have a good absorption of the ink solvents the receiving layer should have a hydrophilic character. The water insoluble polymers used in this invention are both characterised by their insolubility in water and their property to have a hydrophilic character. This hydrophilic character is shown by the water absorbance of these polymers, which should be between at least 0.5% and about 20%. This % refers to the mass of water per mass of polymer; it does not necessarily correspond to the water uptake capability of the microporous membrane. A higher water absorbance of more than about 20% is detrimental for the printed image quality; beading and smearing will be increased.

[0035] The microporous layer of this invention is further characterised by the pore size, the pore shape, the distribution of the various pore sizes over the porous layer or layers, the overall porosity and porosity distribution.

[0036] One of the most important aspects of this invention is the pore size. A pore size of <0.001 micrometer is bad for the ink absorption and a pore size of >1 micrometer is bad for the gloss, ozone fastness and light fastness. The pore size is therefore preferably between 0.001 and 1 micrometer, more preferably between 0.003 and 0.7 micrometer and most preferably between 0.01 and 0.4 micrometer. There is no preference for the pore shape. The pores can be spherical or irregular both are possible. Preferably the pores are interconnected, since this will contributes to a quick ink absorption.

[0037] Preferably, the pore sizes are not homogeneously distributed over the porous layer. It is known in the art, that porous structures tend to have a matte appearance. In order to improve the gloss of microporous materials, the pore size at the top on which the ink is printed, should be small, *viz.* preferably between 0.001 and 0.01 micrometer. The thickness of this top layer should be limited as the ink absorption speed will be negatively influenced when the top layer is too thick. This top layer is preferably between 0.01 and 2 micrometer and more preferably between 0.1 and 1 micrometer. The layer below the top layer viz. the bottom layer should have a bigger average pore size when compared to the top layer in order to enhance the ink absorption. The pore size in this layer is preferably between 0.01 and 1 micrometer.

[0038] A large number of small pores will also have a negative influence on the gloss, so therefore there is also a limitation on the porosity of the top layer. Said porosity should not be over 50% and is preferably between 10 and 50%.

The bottom layer on the contrary should have a high porosity viz. between 30 and 95% in order to have a quick ink absorption. The porosity of the bottom layer is preferably higher than that of the top layer. The porosity can be measured by Mercury Porosimeter ("Autopore IV9500", by Shimadzu Seisakusho).

[0039] The microporous layer as described above is said to be composed of a top layer and a bottom layer. This top and bottom layer may be formed in one single step by which the chemical composition of the top and bottom layer is the same. The top and bottom layer can also have a different chemical composition. Furthermore there may be even more than 2 microporous layers, as long as the top layer has a more small average pore size and a more small porosity than the bottom layers as described above.

[0040] In a further embodiment of this invention it is preferred to use in addition to the water non soluble polymers a certain amount of water soluble polymers. The amount of a water-soluble polymers in the invention is preferably 1 to 40 % by mass, more preferably 2 to 33 % by mass based on the weight of the porous layer.

[0041] These water soluble polymers can be introduced in the microporous structure by various methods. They can for example be present during the formation of the microporous structure, or they can be added by impregnating or coating after the microporous structure is formed.

[0042] Examples of these water soluble polymers are: polyvinyl alcohol (PVA), acetoacetyl-modified polyvinyl alcohol, cation-modified polyvinyl alcohol, anion-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol, polyvinyl acetal and the like] a cellulose-based resin [methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose and the like], chitins, chitosans, starches, ether bond-carrying reins [polyoxyethylene oxide (PEO), polypropylene oxide (PPO), polyethylene glycol (PEG), polyvinyl ether (PVE) and the like], a carbamoyl group-carrying resin [polyacrylamide (PAAM), polyvinyl pyrrolidone (PVP), polyacrylic acid hydrazide and the like], polyacrylates having carboxyl groups as free groups, maleic acid resins, alginates, gelatins, modified gelatins, natural polysaccharide, carrageenan for example, can be used as well. From mentioned polymers, polyvinyl alcohol resin, cellulose resin, ether-group-containing resin, carbamoyl-group-containing resin, carboxyl-group-containing resin, gelatine and carrageenan or mixtures thereof are preferred.

Among the preferred polymers, polyvinyl alcohol-based polymers are especially preferred. Such polyvinyl alcohol polymers may for example be selected from those described in EP-A-1 437 229 and references mentioned in this patent. Furthermore, WO-A-03/054029 describes PVA-NVF copolymer compounds which gives very good results.

[0043] Other preferred water soluble polymers can be selected from the group of modified and unmodified gelatin. These compounds are described amongst others in WO2004/110775, pages 6 and 7. Preferably gelatin compounds in which at least part of the NH_2 groups is chemically modified are used. This modification is done via a condensation reaction with a compound having at least one carboxylic group as described among others in DE-A-19721238. Especially preferred is dodecenylsuccinic acid modified gelatin. Particularly suitable modified gelatins are available under the trade name Imagel™ for example Imagel MA.

[0044] Yet other modified gelatins known in the common gelatin technology, such as phtalated gelatins and acetylated gelatins can also suitably be used.

[0045] Examples of the water-soluble polymers other than the polyvinyl alcohol-based polymers and gelatine are the compounds listed JP-A-11-165461 in paragraph number [0011] to [0014].

[0046] Any of these water-soluble polymers may be employed alone or in combination with each other.

[0047] The receiving layer of the recording medium of this invention can comprise a further layer or further layers between the porous layer and the substrate, which are not microporous. This so called underlayer or these underlayers typically comprise at least one water soluble polymer or a mixture of water soluble polymers. Water soluble polymers which are suitable can be selected from (modified) gelatin, PVA-based polymers, such as fully hydrolysed or partially hydrolysed polyvinyl alcohol (PVA), carboxylated PVA, acetoacetylated PVA, quaternary ammonium modified PVA, copolymers and terpolymers of PVA with other polymers, watersoluble cellulose derivatives such as alkyl cellulose (e.g. methyl cellulose), hydroxyalkyl cellulose (e.g. hydroxyethyl cellulose or hydroxypropyl cellulose), carboxyalkyl cellulose (e.g. carboxymethylalkyl cellulose), dextrin, casein, gum arabic, dextran, polyacrylic acid and its copolymers or terpolymers, polymethylacrylic acid and its copolymers or terpolymers, and any other polymer, which contain monomers of carboxylic acids such as acrylic acid, methacrylic acid, maleic acid and crotonic acid, polyvinylpyrolidone (PVP), polyethylene oxide, polyacrylamide, polymers of 2-pyrrolidone and its derivatives such as N-(2-hydroxyethyl)-2-pyrrolidone and N-cyclohexyl-2-pyrrolidone, urea and its derivatives such as imidazolidinyl urea, diazolidinyl urea, 2-hydroxyethylethylene urea, and ethylene urea.

[0048] The quantity of this at least one water soluble polymer or mixture of water soluble polymers used in the underlayer is preferably from 0.2 to 30.0 g/m^2, more preferably from 0.4 to 17.0 g/m^2. Although in one aspect of the present invention the porous surface layer exhibits an acceptable gloss and has good drying properties it is possible that for the purpose of improved gloss, or in general to improve surface characteristics, the microporous layer is impregnated with a gelatin solution. For this impregnation each gelatin mentioned before might be used although there is a preference for gelatins which have a low molecular weight or a low viscosity. This is important to realise an impregnated layer which is still microporous.

[0049] In a further embodiment of this invention a mordant can be present in the receiving layer. in order to improve the water resistance of the image formed and the anti-blurring ability over a prolonged period. This mordant can be present in any sub layer of the receiving layer. Although the mordant can be present in any layer of the receiving layer, the preferred position is within the porous layer. Surprisingly not the top layer is the best layer, but the mordant should preferably be present just below the top layer, *viz*. in the bottom layer of the microporous layer.

[0050] The mordant is preferably a cationic polymer as an organic mordant (cationic mordant) or an inorganic mordant. The mordant undergoes, when present in the receiving layer, an interaction with a liquid ink containing an anionic dye, whereby stabilizing the dye and improving the water resistance and the anti-blurring ability over a prolonged period. The organic and inorganic mordants may be employed alone independently or in combination with each other.

[0051] A cationic mordant described above is preferably a polymeric mordant having a primary to tertiary amino group or a quaternary ammonium base as a cationic group, and a cationic non-polymeric mordant may also be employed. Such a polymeric mordant is preferably a homopolymer of a monomer (mordant monomer) having a primary to tertiary amino group or a salt thereof, or a quaternary ammonium base, as well as a copolymer or a condensation polymer of such a mordant monomer with other monomers Such a polymeric mordant may be in the form either of a water-soluble polymer or a water-dispersible latex particle.

[0052] An extensive list of organic and inorganic mordants is described in EP-A-1 437 229 paragraph 0088 to paragraph 107. These mordants are included in this invention.

The amount of mordant in the receiving layer is preferably from 0.01 g/m^2 to 5 g/m^2, more preferably from 0.1 g/m^2 to 3 g/m^2.

[0053] In a further embodiment, the receiving layer comprises a super absorber polymer(SAP). In this invention SAP is defined as a polymer which water absorbing capacity is 50-1000 times its dry weight. The water absorbing capacity is measured by soaking for 24 hours at 25 °C, 1 atmosphere. An amount of SAP particles in demineralised water, measure the weight after 24 hours and compare that with the weight before soaking. The water used to determine the absorbing capacity is purified water, meaning water of which most of the ions have been removed by membrane filtration, typically having a conductivity of < 1 micro-siemens.

[0054] Examples of superabsorbers are described in JP57-173194 and JP58-024492, both patent are included herewith in this invention.

[0055] The superabsorbers more specifically can be selected from sodium polyacrylate, lithium polyacrylate, potassium polyacrylate, vinylalcohol-acrylamide copolymer, sodium acrylate-acrylamide copolymer, cellulose polymer, isobuthylene-maleic acid anhydride copolymer, vinylalcohol-acrylic acid copolymer, modified polyethylene oxide, polydiallyldimethylammonium salt, polyacrylate quarternary ammonium salt, sodium polymethacrylate, lithium polymethacrylate, potassium polymethacrylate, vinylalcohol-methacrylamide copolymer, sodium methacrylate-acrylamide copolymer, sodium acrylate-methacrylamide copolymer, sodium methacrylate-methacrylamide copolymer, vinylalcohol-metacrylic acid copolymer, polymethacrylate quarternary ammonium salt, or combinations thereof. Polyacrylic acid and/or its salt, polymethacrylic acid and/or its salt and acrylamide copolymer are preferred superabsorbers.

[0056] The superabsorbers are preferably added as particles of which the particle size is preferably from 0.01 to10 micrometer, more preferably from 0.02 to 5 micrometer and most preferably from 0.03 to 2 micrometer. The amount used is preferably from 1 to 70 g/m2, more preferably from 2 to 50 g/m^2 and most preferably from 3 to 30 g/m^2.

[0057] The SAP can be added in any part of the receiving layer, however best result are obtained when the SAP is added in the underlayer, below the micro-porous layer.

[0058] The receiving layer of the invention preferably contains a cross linking agent capable of cross linking the water-soluble polymers. The cross linking agent may be selected from borax, boric acid, borate, and the like; or such as aldehyde compounds, such as formaldehyde, glyoxal, glutaraldehyde and the like; a ketone-based compound such as diacetyl, cyclopentanedione and the like; an activated halide such as bis(2-chlorethylurea)-2-hydroxy-4,6-dichloro-1,3,5-triazine, 2,4-dichloro-6-S-triazine sodium salt and the like; an activated vinyl compound such as divinylsulfonic acid, 1,3-vinylsulfonyl-2-propanol, N,N'-ethylenebis(vinylsulfonylacetamide), 1,3,5-triacryloylhexahydro-S-triazine and the like; an N-methylol compound such as dimethylol urea, methylol dimethylhydantoin and the like; a melamine resin (for example, methylol melamine, alkylated methylol melamine); an epoxy resin; an isocyanate compound such as 1,6-hexamethylene diisocyanate and the like; aziridine compound described in US-A-3 017 280 and US-A-2 983 611; a carboxyimide compound described in US-A-3 100 704; an epoxy-based compound such as glycelol triglycidyl ether and the like; an ethyleneimino-based compound such as 1,6-hexamethylene -N,N'-bisethyleneurea and the like; a halogenated carboxyaldehyde-based compound such as mucochloric acid, mucophenoxychloric acid and the like; a dioxane-based compound such as 2,3-dihydroxydioxane and the like; a metal-containing compound such as titanium lactate, aluminum sulfate, chromium alum, potassium alum, zirconyl acetate, chromium acetate and the like, a polyamine compound such as tetraethylene pentamine, a hydrazide compound such as adipic acid dihydrazide, a low molecular weight compound or polymer having two or more oxazoline group and the like.

[0059] Any of the crosslinking agents described above may be employed alone or in combination with each other.

The amount of a crosslinking agent employed is preferably 1 to 50% by mass, more preferably 5 to 40% by mass based on a water-soluble polymer.

[0060] The receiving layer of this invention may further comprise microparticles. These microparticles are generally used in an amount of more than 50% by weight or more, preferably more than 60% by weight. The amount by weight as used herein means the amount based on the constituents of the receiving layer other than water. The usage of the micro particles will further improve the drying speed of the receiving layer, but might negatively influence the gloss of the recording medium. The majority of the particles are therefore preferably added in the underlayer and/or the bottom layer of the porous layer. Micro particles which advantageously can be used including the sizes are described for example in EP-A-1 437 229, in particular it may be organic microparticle or inorganic, but is preferably an inorganic microparticle in view of the ink absorption performance and the image stability. A suitable organic microparticle may be a polymeric microparticle obtained by an emulsion polymerization, microemulsion system polymerization, soap-free polymerization, seed polymerization, dispersion polymerization, suspension polymerization and the like, and is typically a powder of a polyethylene, polypropylene, polystyrene, polyacrylate, polyamide, silicon resin, phenol resin, naturally-occurring polymer and the like, as well as a polymeric microparticle in the form of a latex or emulsion. An inorganic microparticle may be a silica microparticle, colloidal silica, titanium dioxide, barium sulfate, calcium silicate, zeolite, kaolinite, halloysite, mica, talc, calcium carbonate, magnesium carbonate, calcium sulfate, pseudo-boehmite, zinc oxide, zinc hydroxide, alumina microparticle, aluminum silicate, calcium silicate, magnesium silicate, zirconium oxide, zirconium hydroxide, cerium oxide, lanthanum oxide, yttrium oxide and the like. Among those listed above, a silica microparticle, colloidal silica, alumina microparticle and pseudo-boehmite are preferred in view of an ability of producing a satisfactory porous structure. A microparticle may be employed as a primary particle or in a form of a secondary particle. The mean primary particle size of any of these microparticle is preferably 2 μm or less, more preferably 200 nm or less.

[0061] More preferably, a silica microparticle whose mean primary particle size is 20 nm or less, a colloidal silica whose mean primary particle size is 30 nm or less, an alumina microparticle whose mean primary particle size is 20 nm or less or a pseudo-boehmite whose mean pore radius is 2 to 15 nm are employed, with the silica microparticle, alumina microparticle and pseudo-boehmite being particularly preferred.

[0062] As a silica microparticle employed in the invention, a gas phase process silica is especially preferred.

[0063] A gas phase process silica described above is different from a hydrated silica in the surface silanol group density and the porosity, and thus exhibits different characteristics, and is suitable for forming a three dimensional structure of a high % void volume.

[0064] Since a gas phase process silica described above has an especially large specific surface area, it exhibits a high efficiency in absorbing and retaining an ink, and also since it has a low refractive index it can impart a receiving layer with a transparency if it is dispersed until achieving an appropriate particle size whereby giving a high color intensity and a satisfactory color development performance. The transparency of the receiving layer is important not only in the use which requires the transparency such as the use as an OHP sheet but also in the use as a printing sheet such as a photo-glossy paper which intends to obtain a high color intensity and a satisfactorily developed color gloss.

[0065] The mean particle size of any of a gas phase process silica described above is preferably 30 nm or less, more preferably 20 nm or less, particularly 10 nm or less, especially 3 to 10 nm. Since the gas phase process silica described above readily undergoes the adhesion between the particles via hydrogen bonds derived from the silanol groups, it can form a structure having a high % void volume when the mean primary particle size is 30 nm or less, whereby improving the ink absorption performance effectively.

[0066] A silica microparticle may be used in combination with other microparticles described above. When using a gas phase process silica in combination with such other microparticles, the gas phase process silica content in the total of the microparticles is preferably 30% by mass, more preferably 50% by mass.

[0067] An inorganic microparticle of the invention is preferably an alumina microparticle, alumina hydrate, mixtures or composite thereof. Among these, the alumina hydrate is preferable because it absorbs and fixes an ink satisfactorily, with a pseudo-boehmite ($Al_2O_3.nH_2O$) being particularly preferred. *n* is an integer of 1 to 8. While the alumina hydrate may be in any form, a sol boehmite is employed preferably as a starting material since it allows a smooth layer to be obtained easily.

[0068] With regard to the microporous structure of a pseudo-boehmite, the mean micropore radius is preferably 1 to 30 nm, more preferably 2 to 15 nm. The micropore volume is preferably 0.3 to 2.0 ml/g, more preferably 0.5 to 1.5 ml/g. The micropore radius and the micropore volume mentioned here are measured in accordance with a nitrogen adsorption/desorption method for example by using a gas adsorption/desorption analyzer (for example, a trade name Omnisorp™ 369 manufactured by Coulter).

[0069] Among various alumina microparticles, a gas phase process alumina microparticle is preferable because of its large specific surface area. The mean primary particle size of said gas phase process alumina microparticle is preferably 30 nm or less, more preferably 20 nm or less.

[0070] When a microparticle is employed in an ink jet printing paper, it can be employed preferably also in the forms disclosed in JP-A-10-81064, JP-A-10-119423, JP-A-10-157277, JP-A-10-217601, JP-A-11-348409, JP-A-2001-138621,

JP-A-2000-43401, JP-A-2000-211235, JP-A-2000-309157, JP-A-2001-96897, JP-A-2001-138627, JP-A-11-91242, JP-A-8-2087, JP-A-8-2090, JP-A-8-2091, JP-A-8-2093, JP-A-8-174992, JP-A-11-192777, JP-A-2001-301314 and the like. The above-mentioned microparticles can be used alone or in combination.

[0071] To be more specific, organic micro particles can be selected for example from polymeric microparticle obtained by an emulsion polymerization, microemulsion system polymerization, soap-free polymerization, seed polymerization, dispersion polymerization, suspension polymerization and the like, and is typically a powder of a polyethylene, polypropylene, polystyrene, polyacrylate, polyamide, silicon resin, phenol resin, naturally-occurring polymer and the like, as well as a polymeric microparticle in the form of a latex or emulsion.

[0072] Inorganic microparticles according to this invention can be selected for example from a silica microparticle, colloidal silica, titanium dioxide, barium sulfate, calcium silicate, zeolite, kaolinite, halloysite, mica, talc, calcium carbonate, magnesium carbonate, calcium sulfate, pseudo-boehmite, zinc oxide, zinc hydroxide, alumina microparticle, aluminum silicate, calcium silicate, magnesium silicate, zirconium oxide, zirconium hydroxide, cerium oxide, lanthanum oxide, yttrium oxide and the like. Among those listed above, a silica microparticle, colloidal silica, alumina microparticle and pseudo-boehmite are preferred in view of an ability of assisting the drying speed. The mean particle size of any of these microparticle is preferably 2 micrometer or less, more preferably 200 nm or less. Also particles with a mean size of 30 nm or less, can be used.

[0073] The receiving layer may further comprise the following ingredients:

- One or more plasticizers, such as (poly)alkylene glycol, glycerol ethers and polymer lattices with low Tg-value such as polyethylacrylate, polymethylacrylate and the like.
- One ore more conventional additives, such as, biocides, pH controllers, preservatives, viscosity modifiers cq stabilisers, dispersing agents, UV absorbing agents, brightening agents, anti-oxidants, light stabilising agents, antistatic agents and/or anionic, cationic, non-ionic, and/or amphoteric surfactants whitening agents, initiators, inhibitors, anti-blurring agents, antifoam agents, matting agents, anti-curling agents, water resistance-imparting agents and the like in accordance with the objects to be achieved.

[0074] The above-mentioned additives (plasticizers, conventional additives) may be selected from those known to a person skilled in the art and may be added in a range of preferably from 0.01 to 10 g/m^2. Any of the components mentioned above may be employed alone or in combination with each other. They may be added after being solubilized in water, dispersed, polymer-dispersed, emulsified, converted into oil droplets, or may be encapsulated in microcapsules.

[0075] The total weight of the applied receiving layer is preferably from 1 to 100 g/m^2, more preferably from 3 to 60 g/m^2 and most preferably from 5 to 40 g/m^2.

[0076] The thickness of the receiving layer is from 2 to 200 micrometer, preferably from 5 to 100 micrometer and most preferably from 10 to 60 micrometer.

[0077] An important characteristic feature of the polymers or combination of polymers of this invention is their solubility in glycerine. As well known to those in the art glycerine is often an important element in ink compositions. It is believed, that the dyes of the ink can be protected by the partly dissolved polymer. The solubility of the polymer or combination of polymers in glycerine is measured by soaking for 24 hours at 25 °C, 1 atm, a piece of polymer film with the size of 1cm x 1cm x 1mm in demineralised water, measure the weight after 24 hours and compare that with the weight before soaking. Preferably the weight increase is from 0.1-10 g/kg, more preferably 0.2-8 g/kg, most preferably 0.3-5 g/kg.

[0078] As mentioned before the water insoluble polymers of the present invention should have a certain water absorption. The water absorption can be measured by soaking a piece of (non micro porous) polymer film with a size of 1cm x 1cm x 1mm in demineralised water for 24 hours at 25 °C, 1 atm, followed by measuring the weight after 24 hours and compare that with the weight before soaking. The water absorption is in general between 0.5 and 20%, more preferably between 0.7 and 15% and most preferably between 0.9 and 10%.

[0079] The contact angle is an important characteristic of the surface of the recording medium of this invention. It is a well known parameter, which gives an indication of the wet ability of the surface to be printed.

[0080] The contact angle is measured by applying at 25 °C, 1 atm a drop of 50 picolitre of demineralised water from 1cm above the receiving layer onto the receiving layer and measure the contact angle at 1 mili second after the droplet touched the layer. The contact angle for the recording media of this invention is generally between 5° and 50°, more preferably between 5° and 30° degree and most preferably between 5° and 25°.

[0081] The support of the present invention can be a transparent support made from a transparent material such as a plastic, or a non-transparent support made from a non-transparent material such as a paper.

A material which can be used as a transparent support described above is preferably a material which is transparent and can to a certain extend resist the heat, when used as overhead sheet in an overhead projector or backlight displaying applications. Such a material may include polyesters such as a polyethylene terephthalate (PET); polysulfones, polyphenylene oxides, polyimides, polycarbonates, polyamides and the like. Among those listed above, polyesters are employed preferably, with a polyethylene terephthalate being preferred especially.

[0082] The thickness of a transparent support mentioned above is not limited particularly, and is preferably 50 to 200 μm for the purpose of easy handling.

[0083] A highly glossy non-transparent support is preferably one whose gloss degree of the surface on the side provided with a colorant-receiving layer is 40% or higher. Such a gloss degree is a value obtained in accordance with the method prescribed in JIS P-8142 (75° mirror surface gloss test of papers and sheets). Typically such support may be for example be a highly glossy paper support such as an art paper, coat paper, cast-coat paper and baryta paper employed for example as a silver halide photograph support; a highly glossy film obtained by adding a white pigment and the like to a plastic film of a polyester such as a polyethylene terephthalate (PET), cellulose esters such as nitrocellulose, cellulose acetate, cellulose acetate butyrate and the like, polysulfone, polyphenylene oxide, polyimide, polycarbonate, polyamide and the like, to make said film opaque (with or without calendering); or a support having a coating layer of a polyolefin which may or may not contain a white pigment over the surface of any of the above-mentioned various paper supports, transparent supports or white pigment-containing highly glossy films. Examples of other supports which may be advantageously used are: a white pigment-containing foamed polyester (for example, a foamed PET obtained by adding a polyolefin microparticle and extending to form voids) or a resin coated paper employed in a silver halide photographic paper.

[0084] While the thickness of a non-transparent support is not limited particularly, it is preferably between 50 to 300 μm for the purpose of easy handling.

[0085] As already mentioned an important characteristic of the inkjet recording medium is the gloss. It has been found that the gloss of the medium can be improved by selecting the appropriate surface roughness of the used support. It was found, that providing a support having a surface roughness characterised by the value Ra being less than 1.0 μm, preferably below 0.8 μm a very glossy medium can be obtained. A low value of the Ra indicates a smooth surface. The Ra is measured according to DIN 4776; software package version 1.62 with the following settings:

(1) Point density 500 P/mm (2) Area 5.6 x 4.0 mm^2 (3) Cut-off wavelength 0.80 mm (4) Speed 0.5 mm/sec., using a UBM equipment.

[0086] In case paper is used as the support for the present invention the paper is selected from materials conventionally used in high quality printing paper. Generally it is based on natural wood pulp and if desired, a filler such as talc, calcium carbonate, TiO_2, $BaSO_4$, and the like can be added. Generally the paper also contains internal sizing agents, such as alkyl ketene dimer, higher fatty acids, paraffin wax, alkenylsuccinic acid, such as epichlorhydrin fatty acid amid and the like. Further the paper may contain wet an dry strength agents such as a polyamine, a poly-amide, polyacrylamide, poly-epichlorohydrin or starch and the like. Further additives in the paper can be fixing agents, such as aluminium sulphate, starch, cationic polymers and the like. The Ra value for a normal grade base paper is well below 2.0μm and may typically have values between 1.0 and 1.5 μm. The receiving layer or layers of the present invention can be directly applied to this base paper.

[0087] In order to obtain a base paper with a Ra value below 1.0 μm such a normal grade base paper can be coated with a pigment. Any pigment can be used. Examples of pigments are calcium-carbonate, TiO_2, $BaSO_4$, clay, such as kaolin, styrene-acrylic copolymer, Mg-Al-silicate, and the like or combinations thereof. The amount being between 0.5 and 35.0 g/m^2 more preferably between 0.5 and 20.0 g/m^2. This pigmented coating can be applied as a pigment slurry in water together with suitable binders like styrene-butadiene latex, methyl methacrylate-butadiene latex, polyvinyl alcohol, modified starch, polyacrylate latex or combinations thereof, by any technique known in the art, like dip coating, roll coating, blade coating or bar coating. The pigment coated base paper may optionally be calendered. The surface roughness can be influenced by the kind of pigment used and by a combination of pigment and calendering. The base pigment coated paper substrate has preferably a surface roughness between 0.4 and 0.8 μm. If the surface roughness is further reduced by super calendaring to values below 0.4 μm the thickness and stiffness values will in general become below an acceptable level.

[0088] The receiving layer or layers of the present invention can be directly applied to the pigment coated base paper.

[0089] In another embodiment, the pigment coated base paper having a pigmented top side and a back-side is provided on both sides with a polymer resin through high temperature co-extrusion giving a laminated pigment coated base paper. Typically temperatures in this (co-) extrusion method are above 280 °C but below 350 °C. The preferred polymers used are poly olefins, particularly polyethylene. In a preferred embodiment the polymer resin of the top side comprises compounds such as an opacifying white pigment *e.g.* TiO_2 (anatase or rutile), ZnO or ZnS, dyes, coloured pigments, including blueing agents, e.g.ultramarine or cobalt blue, adhesion promoters, optical brighteners, antioxidant and the like to improve the whiteness of the laminated pigment coated base paper. By using other than white pigments a variety of colors of the laminated pigment coated base paper can be obtained. The total weight of the laminated pigment coated base paper is preferably between 80 and 350 g/m^2. The laminated pigment coated base paper shows a very good smoothness, which after applying the (ink) receiving layer or layers of the present invention results in a recording medium with excellent gloss. On the other hand, depending on the product one wants to make a polyethylene-coated paper can be used with a matt surface or silky surface such as well known in the art. Such a surface is obtained by conducting an embossing treatment upon extruding a polyethylene on a paper substrate.

[0090] The microporous layer of this invention can be made using various techniques as described for example in JP2001-519733, JP10-114146, where a description is given of the so-called "immersion precipitation" and a method comprising the steps of :

1: coating on a support at least one selected from the group of polymer solution, polymer suspension, monomer solution, monomer suspension, oligomer solution and oligomer suspension;
2: Polymerising and/or cross-linking the substances mentioned under 1,
3: Drying the coated support.

[0091] Further methods of making a porous layer are described in for example US-A-4 642 247.

[0092] Any of the methods described in the above references can be used, to make the media of this invention. The porous layer of this invention can be a single layer or a multi-layer as described above. It can be produced in one single step or in successive steps as long as the preferred pore sizes, pore size distribution and porosity resp. porosity distribution is obtained.

[0093] As a coating method, any methods can be used. For example, curtain coating, extrusion coating, air-knife coating, slide coating, roll coating method, reverse roll coating, dip coating, rod bar coating.

[0094] Before applying the coating to the surface of the support material described above this support may be subjected to a corona discharge treatment, glow discharge treatment, flame treatment, ultraviolet light irradiation treatment and the like, for the purpose of improving the wet ability and the adhesiveness.

[0095] The recording media of the present invention can be used for a multitude of recording applications so it is within the scope of the present invention to provide recording media that are suitable for creating high quality images by using techniques as for example Giclée printing, colour copying, screen printing, gravure, dye-sublimation, flexography, ink jet and the like.

[0096] The media described in this invention are particularly usefull in ink jet application.

[0097] Although any kind of ink can be used very good results are obtained with inks described in for example US2005001890.

[0098] The dyes preferably used in the ink jet applications of this invention are dyes having an oxidation potential(Eox) more positive than 1.1 V (vs SCE, saturated calomel electrode), more preferably more positive than 1.15 V (vs SCE), and most preferably more positive than 1.2 V (vs SCE).

The Eox can be easily measured by a person skilled in the art. The method is described, for example, in P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers (1954), A. J. Bard et al., Electrochemical Methods, John Wiley & Sons (1980), and Akira Fujishima et al., Denkikagaku Sokutei Ho (Electrochemical Measuring Methods), Gihodo Shuppan Co., Ltd. (1984).

[0099] More specifically, a test sample is dissolved at a concentration of $1 \cdot 10^{-2>}$ to $1 \cdot 10^{-6}$ mol/liter in a solvent such as dimethylformamide or acetonitrile containing a supporting electrolyte such as sodium perchlorate or tetrapropylammionium perchlorate and the oxidation potential is measured as a value to SCE using various methods for voltammetry. The value sometimes deviates on the order of several tens of millivolts due to the effect of liquid junction potential, liquid resistance of sample solution, or the like, but reproducibility of the potential can be guaranteed by calibration using a standard sample (for example, hydroquinone).

[0100] In order to univocally specify the potential, in the present invention, a value (vs SCE) measured in dimethylformamide (concentration of dye 0.001 mol dm^{-3}) containing 0.1 mol dm^{-3} of tetrapropylammonium perchlorate as the supporting electrolyte is used as the oxidation potential of the dye.

The Eox value indicates the transferability of an electron from the sample to the electrode and as the value is larger (the oxidation potential is more positive), the electron is less transferable from the sample to the electrode, in other words, the oxidation occurs less. As for the relationship with the structure of compound, the oxidation potential becomes more positive when an electron-withdrawing group is introduced, and becomes more negative when an electron-donating group is introduced. In the present invention, the oxidation potential is preferably rendered more positive by introducing an electron-withdrawing group into the dye skeleton so as to reduce the reactivity with ozone that is an electrophilic agent.

[0101] As for the type of dye which can be used in the ink composition, the following structure is preferred.

$$(\mathrm{Ch})\text{-}(\mathrm{EWG})_n$$

[0102] Here, Ch represents a chromophore containing unsaturated heterocyclic group, EWG represents substituent electron-withdrawing group with the Hamett substituent constant is more than 0.40, and *n* represents integers between

1 and 8.

[0103] Examples for Ch are; azo dyes, phtalocyanine dyes, azomethine dyes, quinine dyes (*e.g.* anthraquinone, anthrapyridone), carbonium dyes (ex. triphenylmethane dyes, xyanthane dyes, acrydine dyes), azine dyes (ex. oxazine, thiazine), more preferably azo dyes, phtalocyanine dyes, azomethine dyes and anthrapyridone, most preferably azo dyes and phtalocyanine dyes.

[0104] The present invention will be illustrated in more detail by the following non-limiting examples. Unless stated otherwise, all ratios given are based on weight.

Examples

(Preparation of coating composition A)

[0105] A bovine bone gelatine (1:1:1 mixture of PB88210(PB), P3201(Nitta) and 69829 (Gelita)) was dissolved in water to make a 10% solution. The pH was adjusted to 6.0 ± 0.1.

(Preparation of coating composition B)

[0106] Cellulose di-acetate was dissolved in acetone to make 10% solution.

(Preparation of coating composition C)

[0107] 175 g of polyamide 6-3-T (Trogamid T-5000, supplied by Degussa) was dissolved in 550 g of N-methylpyrrolidone and 280 g of diethyleneglycol.

(Preparation of coating composition D)

[0108] Pig skin acid gelatine (mw 10K) was dissolved in water to make 5% solution.

(Preparation of coating composition E)

[0109] Polyvinylalcohol (Mowiol 4-88, supplied by Kuraray) was dissolved in water to make 5% solution.

(Preparation of coating composition F)

[0110] 170 g of polyamide 6-3-T (Trogamid T-5000, supplied by Degussa) and 5 g of polyvinylpyrridine were dissolved in a mixture of 550 g of N-methylpyrrolidone and 280 g of diethyleneglycol.

(Preparation of coating composition G)

[0111] 165 g of polyamide 6-3-T (Trogamid T-5000, supplied by Degussa) and 10 g of polyvinylpyrridine were dissolved in a mixture of 550 g of N-methylpyrrolidone and 280 g of diethyleneglycol.

(Preparation of coating composition H)

[0112] 100 g of super absorbent polymer mainly composed of polyacrylic acid (AQUAKEEP, mean particle size 10 micrometer, supplied by Sumitomo Seika) was dispersed in a solution in which 50 g of PVP (Mw = 30K) was dissolved in 850 g of iso-propanol.

(Preparation of coating composition I)

[0113] 2,4-dichrolo-6-S-triazine sodium salt was added as crosslinker to the coating composition D so that the amount of the compound was 2 wt% of the total gelatine.

(Preparation of coating composition J)

[0114] 40 g of fumed silica (Reosiel QS-30, mean primary particle size 7nm, supplied by Tokuyama) was added to the coating composition C and dispersed.

(Preparation of coating composition K)

[0115] 40 g of fumed silica (Reosiel QS-30, mean primary particle size 7nm, supplied by Tokuyama) was added to the coating composition G and dispersed.

(Preparation of coating composition L)

[0116] 38 g of epoxy diacrylate (CN132, supplied by Cray Valley) and 1.5 g of photo initiator (Irgacure 2959, supplied by Ciba Specialty Chemicals) were dissolved in the mixed solvent of 50.5 g of water and 10 g of iso-propanol.

(Preparation of coating composition M)

[0117] 2 g of vinylpyrridine and 4 g of PVA (Mowiol 4-88, supplied by Kuraray) were added to the coating composition L.

(Preparation of coating composition N)

[0118] 2 g of PVA (Mowiol 4-88, supplied by Kuraray) was added to the coating composition L.

(Preparation of coating composition O)

[0119] 100 g of fumed silica (average size of primary particles: 7 nm, BET surface area: 300 m^2/g), 4 g of dimethylarylammoniumchloride homopolymer (Sharol DC902P, supplied by Daiichi Kyogyo Seiyaku), 24 g of polyvinyl alcohol (PVA235, supplied by Kuraray), 5 g of boric acid, 0.3 g of surfactant (Swanol AM-2150, supplied by Nihon surfactant) and 2 g of basic polyhydroxyaluminium (Purachem WT, supplied by Riken Green) were dispersed and dissolved in 1220 g of water. The pH was adjusted to 6.0 ± 0.1.

[Preparation of recording medium R-1]

[0120] Onto a Polyethylene (PE) laminated base paper, which had been corona treated, coating composition A was coated with 200 cc/m^2. The coated substrate was immediately immersed in a pure ethanol bath at 20 °C. A microporous layer was formed which was dried at 80 °C for 1h.

[Preparation of recording medium R-2]

[0121] Onto a (PE) laminated base paper, whichhad been corona treated coating composition B was coated with 200 cc/m^2. The coated substrate was immersed immediately in a water bath at 20 °C. A microporous layer was formed, which was dried at 80 °C for 1h.

[Preparation of recording medium R-3]

[0122] Onto a PE laminated base paper, which had been corona treated coating composition C was coated with 115 cc/m^2. The coated substrate was immersed immediately in a water bath at 20 °C. A microporous layer was formed which was dried at 80 °C for 1h.

[Preparation of recording medium R-4]

[0123] Onto substrate R-3, coating composition D was coated with 40 cc/m^2. The resulting medium was dried at 80 °C for 1h.

[Preparation of recording medium R-5]

[0124] Onto substrate R-3 coating composition E was coated with 40 cc/m^2. The resulting medium was dried at 80 °C for 1h.

[Preparation of recording medium R-6]

[0125] Onto a PE laminated base paper, whichhad been corona treated coating composition F was coated with 115 cc/m^2. The coated substrate was immersed immediately in a water bath at 20 °C. A microporous layer was formed which was dried at 80 °C for 1h. On top of the microporous layer composition E was coated with 40 cc/m^2. The resulting medium was dried at 80 °C for 1h

[Preparation of recording medium R-7]

[0126] Onto PE laminated base paper, which had been corona treated coating composition C was coated with 58 cc/m^2, on top of which G was coated with 58 cc/m^2 by a multilayer coating method. The resulting coated substrate was immersed immediately in a pure water bath at 20 °C giving a microporous layer The resulting medium was dried at 80 °C for 1h.

[Preparation of recording medium R-8]

[0127] The steps for the preparation of recording medium R-7 above were repeated, but this time coating composition H was coated with 100 g/m^2 instead of composition C.

[Preparation of recording medium R-9]

[0128] The steps for the preparation of recording medium R-4 above were repeated, but this time coating composition I was used instead of composition D.

[Preparation of recording medium R-10]

[0129] The steps for the preparation of recording medium R-7 above were repeated, but this time coating composition J was used instead of composition C and coating composition K was used instead of composition G.

[Preparation of recording medium R-11]

[0130] Onto PE laminated base paper, which had been corona treated coating composition L was coated with 40 cc/m^2, on top of which M was coated with 40 cc/m^2, on top of which N was coated with 10 cc/m^2, by a multilayer coating method. The resulting coated substrate when still wet was exposed to UV light with a wavelength of 200 to 400nm at 0.4 J/cm^2 using "Light Hammer 6" supplied by Fusion UV Systems giving a microporous structure. The resulting medium was dried at 80 °C for 1h.

[Preparation of recording medium C-1]

[0131] Coating composition O was coated with 270 cc/m^2 and dried at 80 °C for 1h

[Preparation of recording medium C-2]

[0132] The same as R-1, but the immersion process in pure ethanol was skipped, resulting in a swellable medium consisting of gelatin.

[0133] The following items were measured for all the above media.

Pore size: Surface pore size and internal pore size.

[0134] At the temperature of liquid N_2 the medium was broken and using SEM the pores visible at the cross section were evaluated.

[0135] The surface pore size is defined as the average pore size of the pores down to 1 micrometer from the surface, the internal pore size is defined as the average pore size of the pores more than 1 micrometer deep.

Contact angle:

[0136] The contact angle was measured by applying at 25 °C, 1 atm a drop of 50 picolitre of demineralised water from 1 cm above the recording medium onto the receiving layer and measure the contact angle at 1 mili second after the droplet touched the layer.

Drying speed

[0137] For this test the EPSON PM-G820™ printer was used. A 4 cm× 4 cm square was printed black with the highest density. Just after the printing is finished, the 4 corners are wiped with a finger towards the white part of the medium and any smearing is observed.

[0138] Criteria:

A: no smudge at all
B: very slight smudge, no practical problem
C: some smudge
D: severe smudge, not acceptable

Water fastness:

[0139] For this test the EPSON PM-G820™ printer was used. The printed image was a standard chart from Gazou Densi Gakkai. The printed image was dried overnight.

[0140] The printed medium was soaked in water of 20 °C for 30 minutes, after which the density for black, yellow, cyan and mangenta was measured (Cf) and compared with the initial density. The calculated Cf/Ci (initial density) × 100 average for the 4 colors is a measure for the water fastness.

[0141] Criteria:

A: >90%
B: >70%
C: 40-70%
D: <40%

Gloss

[0142] The gloss is measured at 20° using the REFO 3-D REFLEKTOMETER™ supplied by DR LANGE.

Ozone fastness

[0143] The ozone fastness was measured by exposing a test image having black, cyan, yellow and magenta patches of 1.0, 1.5 and 2 initial density to 0.5 ppm of ozone for 48 h. The remaining density divided by the initial density x 100% is a measure for the ozone fastness

[0144] Criteria:

A: >80% for all densities
B: <80% for 1 or 2 densities
C: <80% for all densities

Light fastness

[0145] The light fastness is measured by exposing a test image having black, cyan, yellow and magenta patches of 1.0, 1.5 and 2 initial density to 85,000 lux for 10 days. The remaining density divided by the initial density x 100% is a measure for the light fastness

[0146] Criteria:

A: >70% for all densities
B: <70% for 1 or 2 densities
C: <70% for all densities

[0147] Results are shown in Table 1.

Table 1

	Pore size surface, μm	Pore size internal, μm	Contact angle	Absorption speed	Water fastness	Gloss	Ozone fastness	Light fastness
R-1 invent.	0.1	0.2	20 deg	B	B	70%	B	B
R-2 invent.	0.2	0.6	50 deg	B	B	50%	B	B
R-3 inven.	0.1	0.5	45 deg	B	B	60%	B	B
R-4 invent.	0.05	0.5	20 deg	B	B	75%	A	A
R-5 invent.	0.05	0.5	20 deg	B	B	70%	A	A
R-6 invent.	0.05	0.4	20 deg	B	B	70%	A	A
R-7 invent.	0.05	0.4	20 deg	B	A	70%	A	A
R-8 invent.	0.05	0.2	20 deg	A	A	70%	A	A
R-9 invent.	0.05	0.5	20 deg	B	A	70%	A	A
R-10invent.	0.05	0.2	20 deg	A	A	50%	A	A
R-11invent.	0.05	0.2	15 deg	A	A	70%	A	A
C-1 comp.	0.05	0.04	15 deg	A	C	20%	C	C
C-2 comp.	no pores	no pores	20 deg	C	C	70%	B	C

[0148] From the Table it is clear the recording media of the present invention with the small pores at the surface layer and bigger pores below the surface layer have a good gloss and a good drying speed.

[0149] These results were confirmed upon using:

[0150] The Canon PIXUS8600i^{TM} printer.

[0151] The Hewlett-Packard printer Photosmart 8450^{TM} and

[0152] The Lexmark Printer P915^{TM}.

Claims

1. Recording medium comprising a support and a receiving layer adhered to this support, which receiving layer comprises at least one asymmetric porous layer having a bottom layer and a top layer further away from the support than said bottom layer comprising at least one organic polymer, wherein the average pore size in the bottom layer is larger than the average pore size in the top layer.

2. Medium according to claim 1, wherein the thickness of the top layer is at most 2 micrometer.

3. Medium according to any of the previous claims, wherein the average pore size in the top layer is from 0.001 to 1 μm, preferably between 0.01 and 0.8 micrometer.

4. Recording medium according to any of the previous claims, wherein said at least one organic polymer, is selected from the group of water-non-soluble polymers and polymers which are treated to be water non-soluble.

5. Recording medium according to any of the previous claims, wherein said at least one polymer includes polymers having at least one nitrogen atom in their molecular structure.

6. Recording medium according to any of the previous claims, wherein said at least one organic polymer comprises a water non-soluble polymer selected from the group of cellulose, cellulose acetate, cellulose nitrate, polysulfone, ployethersulfone, polyamide, nylon, polyacrylate, polyesther, polypropylene, PVDF, polycarbonate, polyurethane, polyacrylonitrile, PVC, cross-linked PVA and cross-linked gelatine.

7. Recording medium according to any of the previous claims, comprising a combination of at least one water non-soluble polymer and at least one water-soluble polymer.

8. Recording medium according to claim 7, wherein said at least one water-soluble polymer is selected from the group of polyvinyl alcohol resin, cellulose resin, ether-group-containing resin, carbamoyl-group-containing resin, carboxyl-group-containing resin, gelatine and carrageenan.

9. Recording medium according to the previous claims, wherein the porosity of said top layer is from 10 to 50% and the porosity of said bottom layer is between 30 and 95% and the porosity of said top layer is lower than the porosity of said bottom layer.

10. Recording medium according to previous claims, wherein said receiving layer further comprises at least one mordant.

11. Recording medium according to claim 10, wherein the mordant is located in the porous layer, preferably below the top porous layer.

12. Recording medium according to the previous claims, wherein said receiving layer further comprises at least one kind of super absorbent polymer.

13. Recording medium according to claim 12, wherein the super absorbent polymer is located below the porous layer.

14. Recording medium according to the previous claims, where at least one of said polymers dissolves in glycerine at room temperature in an amount of more than 0.1 g/l and less than 10 g/l.

15. Recording medium according to the previous claims, wherein at least one of said water non soluble polymers absorbs water in an amount of more than 0.5% and less than 20%.

16. Recording medium according to the previous claims, wherein the said receiving layer further comprises at least one kind of micro particle.

17. Recording medium according to Claim 16, wherein the micro particle is selected from the group of silica, colloidal silica, alumina, boehmite and pseudo boehmite.

18. Recording medium according to the previous claims, wherein the porous layer comprises at least 2 layers with different composition.

19. Recording medium according to the previous claims, wherein the support is selected from a base paper, a pigment coated base paper, a base paper with a polymer laminated on either side or both sides, a pigment coated base paper with a polymer laminated on either side or both sides, a synthetic paper and a polymer film.

20. Recording medium according to claim 19, wherein the support has a surface roughness Ra smaller than 1.0 micrometer.

21. Recording method **characterized in that** images or letters are printed onto the recording medium according to claims 1-20, wherein small droplets of ink are ejected using an inkjet printer.

22. Recording method according to claim 21, wherein at least one kind of ink is used including at least one kind of dye with the oxidation potential of more than 1.2 V vs SCE.

23. Recording method according to claim 21, wherein at least two kinds of ink are used in the inkset including at least one kind of dye with the oxidation potential of more than 1.2 V vs SCE.

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EUROPEAN SEARCH REPORT

Application Number
EP 05 07 5692

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Place of search	Date of completion of the search	Examiner
Munich	9 November 2005	Spyropoulou, E

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