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(54) **Ink-jet recording sheet**

(57) The present invention relates to an ink-jet recording sheet comprising a diallyldimethyl cation polymer and at least one member selected from polyallyl amine and polyvinyl amine.

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Description**BACKGROUND OF THE INVENTION****Field of the Invention**

[0001] The present invention relates to a recording material suitable for ink-jet recording using liquid inks such as water-based and oil-based inks, or solid inks, which are solid at an ordinary temperature but are melted and liquefied for printing.

Description of the Related Art

[0002] In recent years, with the rapid advance of the information industry, various information processing systems have been developed. Recording methods and devices suitable for the latest information systems have also been developed and put into practical use.

[0003] Ink-jet recording methods are widely utilized for recording both in offices and homes because various kinds of recording materials can be used. Further, the hardware (devices) used therein are relatively inexpensive, compact, and are remarkably silent.

[0004] Furthermore, higher resolutions in ink-jet printers have made photograph-like high-quality prints a reality. With the advances in hardware (devices), various kinds of recording sheets for ink-jet recording have also been developed.

[0005] The desired traits of an ink-jet recording sheet generally include (1) rapid drying (high ink-absorption rate) ; (2) correct and uniform diameter of ink dots (no blurring) ; (3) good graininess; (4) high dot circularity; (5) high color density; (6) high chroma (without dullness); (7) excellent light resistance and water resistance of image portions; (8) high whiteness of the recording sheet; (9) excellent shelf stability of the recording sheet (i.e., yellowing does not occur during long-term storage); (10) resistance to deformation and good dimensional stability (sufficiently low curling) ; and (11) good running in hardware. Further, in order to obtain photograph-like high-quality prints, the photo glossy paper should possess traits such as good glossiness, surface smoothness, and the photographic paper-like feel similar to that of silver salt photographs in addition to above traits.

[0006] In order to improve these characteristics, an ink-jet recording sheet having a colorant-accepting porous layer has been developed and put into practical use. By virtue of its porous structure, the ink-jet recording sheet has excellent ink absorption (rapid drying) and high glossiness.

[0007] Such ink-jet recording sheets, which use a diallyldimethyl cation polymer as an inhibitor of aggregation of fine inorganic particles, are disclosed in Japanese Patent Application Laid-open (JP-A) Nos. 2001-253165, 8-218279, 63-162275, but fading with time is still a problem and further improvements in glossiness are also required.

[0008] Further, ink jet recording sheets using a polyallyl amine as an organic mordant are disclosed in JP-A Nos. 11-115308 and 10-181190. In the gazette of JP-A No. 11-115308, ammonia is used as an inhibitor of aggregation of fine inorganic particles, but in this case, low print density is a problem.

SUMMARY OF THE INVENTION

[0009] Accordingly, the present invention was made in light of the problem described above, and the object of the invention is to provide an ink-jet recording sheet, which while maintaining high print density, does not fade with time and has high glossiness.

[0010] A first aspect of the invention provides an ink-jet recording sheet comprising a diallyldimethyl cation polymer and at least one selected from a polyallyl amine and a polyvinyl amine.

[0011] A second aspect of the invention provides an ink-jet recording sheet having a colorant-accepting layer on the surface of a substrate, wherein the colorant-accepting layer is a layer prepared by applying a first coating solution containing fine inorganic particles with an average primary particle diameter of 20 nm or less, a water-soluble resin, a diallyldimethyl cation polymer and a cross-linking agent capable of cross-linking the water-soluble resin, followed by cross-linking and curing the coating layer, the cross-linking and curing being conducted by applying a second coating solution containing at least one selected from a polyallyl amine and a polyvinyl amine and at least one selected from a hydrophobic organic acid containing 4 or more carbon atoms and an ammonium salt of the hydrophobic organic acid, onto the coating layer or film, (1) when the first coating solution is applied, (2) while the coating layer formed by applying the first coating solution is dried and before the coating layer's drying rate lapses, or (3) after the coating layer formed by applying the first coating solution is dried to form a film.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

<<Ink-jet recording sheet>>

[0012] The ink-jet recording sheet of the present invention comprises a diallyldimethyl cation polymer and at least one selected from a polyallyl amine and a polyvinyl amine. By using the diallyldimethyl cation polymer in combination with at least one selected from a polyallyl amine and a polyvinyl amine, an ink-jet recording sheet that does not fade with time and that possesses high glossiness and print density can be obtained.

[0013] As described above, the ink-jet recording sheet of the invention contains a diallyldimethyl cation polymer and a polyallyl amine and/or a polyvinyl amine, but may also contain fine inorganic particles, a water-soluble-resin, a cross-linking agent capable of cross-linking the water-soluble resin, and other additives if necessary.

[0014] In a preferable embodiment of the invention, the ink-jet recording sheet comprises a colorant-accepting layer on a substrate, and the colorant-accepting layer preferably contains the respective components described above.

<Colorant-accepting layer>

Diallyldimethyl cation polymer

[0015] The diallyldimethyl cation polymer is used for preventing aggregation of fine inorganic particles, and by using this polymer in combination with a polyallyl amine and/or a polyvinyl amine, an ink-jet recording sheet not only having excellent resistance to blurring with time but having also high glossiness and print density can be obtained.

[0016] Examples of the diallyldimethyl cation polymer include polydiallyldimethyl ammonium chloride, and the diallyldimethyl cation polymer may be a homopolymer of each monomer or a copolymer.

[0017] The diallyldimethyl cation polymer may be a copolymer with other monomers. Examples of the other monomers include nonionic monomers such as alkyl (meth)acrylates (for example, alkyl (meth)acrylates (number of carbon atoms in the alkyl group: 1 to 18) such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate), cycloalkyl (meth)acrylates (for example, cyclohexyl (meth)acrylate), aryl (meth)acrylates (for example, phenyl (meth)acrylate), aralkyl esters (for example, benzyl (meth)acrylate), substituted alkyl (meth)acrylates (for example, 2-hydroxyethyl (meth)acrylate), (meth)acrylamides (for example, (meth)acrylamide, and dimethyl (meth)acrylamide), aromatic vinyl compounds (for example, styrene, vinyltoluene, and α -methylstyrene), vinyl esters (for example, vinyl acetate, vinyl propionate, vinyl versatate etc.), allyl esters (for example, allyl acetate), halogen-containing monomers (for example, vinylidene chloride, and vinyl chloride), vinyl cyanides (for example, (meth)acrylonitrile) and olefins (for example, ethylene, and propylene). These nonionic monomers can be used alone or in combination thereof.

[0018] The molecular weight of the diallyldimethyl cation polymer is preferably 2,000 to 100,000, and more preferably 4,000 to 70,000, in terms of weight average molecular weight. Given a molecular weight of 2,000 or more, the ink-jetting recording sheet can be endowed with more sufficient water resistance, whereas given a molecular weight of 100,000 or less, handling suitability can be maintained more excellently while preventing an extreme increase in viscosity.

[0019] The content of the diallyldimethyl cation polymer is preferably 0.5 to 30 parts by mass, and more preferably 1 to 10 parts by mass, relative to 100 parts by mass of the fine inorganic particles. When the content of the diallyldimethyl cation polymer is in the range of the above-described range, the effect of the invention can be demonstrated more effectively.

[0020] The diallyldimethyl cation polymer is not particularly limited, but the cation polymer of water-soluble or aqueous emulsion type can be preferably used.

[0021] The diallyldimethyl cation polymer can also be used in combination with other cationic polymers. The content of the diallyldimethyl cation polymer when used in combination with other cationic polymers is preferably 50% by mass or more, and more preferably 70% by mass or more, in the whole of the cationic polymers.

[0022] Examples of the other cationic polymers include, for example, dicyan cationic resins represented by dicyan diamide-formalin polycondensates, polyamine cationic resins represented by dicyan amide-diethylene triamine polycondensates, and polycation type cationic resins such as epichlorohydrin-dimethylamine addition polymers, dimethyldiallyl ammonium chloride-SO₂ copolymers, diallylamine salt-SO₂ copolymers, dimethylallyl ammonium chloride polymers, allylamine salt polymers, dialkylaminoethyl (meth)acrylate quaternary salt polymers and acrylamide-diallylamine salt copolymers, and monomethyldiallyl ammonium chloride and polyamidine are preferable, and monomethyl ammonium chloride is particularly preferable from the viewpoint of water resistance. The cationic polymers may be used alone or in combination thereof.

Polyallyl amine, and polyvinyl amine

[0023] The ink-jet recording sheet of the invention contains at least one selected from polyallyl amine and polyvinyl amine (including salts and derivatives thereof) in order to improve resistance to blurring with time, glossiness and print density by using it in combination with the diallyldimethyl cation polymer.

[0024] The polyallyl amine and polyvinyl amine (organic mordant) can interact with liquid ink having an anionic dye as a colorant, thereby stabilizing the colorant and particularly improving water resistance and resistance to blurring with time.

[0025] The molecular weight of the polyallyl amine is preferably 3,000 to 30,000, and more preferably 5,000 to 20,000, in terms of weight average molecular weight. The molecular weight of the polyvinyl amine is preferably 3,000 to 30,000, and more preferably 5,000 to 20,000, in terms of weight average molecular weight. When the molecular weight is in the above-described range, water resistance and resistance to blurring with time can be improved more sufficiently.

[0026] The salts of the polyallyl amine include inorganic acid salts such as a hydrochloride and a sulfate, and organic acid salts such as an acetate, a toluenesulfonate and a methanesulfonate.

[0027] The salts of the polyvinyl amine include salts similar to those of the polyallyl amine described above.

[0028] The derivatives of the polyallyl amine include those in which acrylonitrile, chloromethylstyrene, TEMPO, and/or epoxysiloxane are added to a polyallyl amine in an amount of 2 to 50 mol%, and those in which acrylonitrile and/or chloromethylstyrene are added to a polyallyl amine in an amount of 5 to 10 mol% are preferable, and those in which acrylonitrile is added to a polyallyl amine in an amount of 5 to 10 mol% are more preferable from the viewpoint of exhibiting an inhibitory effect on ozone discoloration.

[0029] The derivatives of the polyvinyl amine are similar to those of the polyallyl amine described above.

[0030] The content of the polyallyl amine or polyvinyl amine (or the total content when both are used in combination) is preferably 1 to 5 parts by mass, and more preferably 1.25 to 3.75 parts by mass, relative to 100 parts by mass of the fine inorganic particles. When the content of the polyallyl amine and the polyvinyl amine is in the above range, the effect of the invention can be demonstrated more effectively.

[0031] The polyallyl amine and polyvinyl amine can also be used in combination with other organic mordants. When used in combination with other organic mordants, the content of the polyallyl amine or polyvinyl amine (or the total content when both are used in combination) is preferably 50% by mass or more, and more preferably 70% by mass or more, in the whole of the organic mordants.

[0032] Polymer mordants having a primary to tertiary amino group or a quaternary ammonium base as the cationic group can be preferably used as the other organic mordants (cationic mordants), but cationic non-polymer mordants can also be used.

[0033] The polymer mordants are preferably homopolymers of monomers (mordant monomers) having a primary to tertiary amino group or a salt thereof or a quaternary ammonium base, or copolymers or polycondensates of the mordant monomer with other monomer (referred to hereinafter as "non-mordant monomer"). These polymer mordants can be used in the form of either water-soluble polymers or water-dispersible latex particles.

[0034] Examples of the monomer (mordant monomer) include, for example, trimethyl-p-vinylbenzyl ammonium chloride, trimethyl-m-vinylbenzyl ammonium chloride, triethyl-p-vinylbenzyl ammonium chloride, triethyl-m-vinylbenzyl ammonium chloride, N,N-dimethyl-N-ethyl-N-p-vinylbenzyl ammonium chloride, N,N-diethyl-N-methyl-N-p-vinylbenzyl ammonium chloride, N,N-dimethyl-N-n-propyl-N-p-vinylbenzyl ammonium chloride, N,N-dimethyl-N-n-octyl-N-p-vinylbenzyl ammonium chloride, N,N-dimethyl-N-benzyl-N-p-vinylbenzyl ammonium chloride, N,N-diethyl-N-benzyl-N-p-vinylbenzyl ammonium chloride, N,N-dimethyl-N-(4-methyl)benzyl-N-p-vinylbenzyl ammonium chloride, N,N-dimethyl-N-phenyl-N-p-vinylbenzyl ammonium chloride, trimethyl-p-vinylbenzyl ammonium bromide, trimethyl-m-vinylbenzyl ammonium bromide, trimethyl-p-vinylbenzyl ammonium sulfonate, trimethyl-m-vinylbenzyl ammonium sulfonate, trimethyl-p-vinylbenzyl ammonium acetate, trimethyl-m-vinylbenzyl ammonium acetate, N,N,N-triethyl-N-2-(4-vinylphenyl)ethyl ammonium chloride, N,N,N-triethyl-N-2-(3-vinylphenyl)ethyl ammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinylphenyl)ethyl ammonium chloride, N,N-diethyl-N-methyl-N-2-(4-vinylphenyl)ethyl ammonium acetate, quaternary products, with methyl chloride, ethyl chloride, methyl bromide, ethyl bromide, methyl iodide or ethyl iodide, of N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide and N,N-diethylaminopropyl (meth)acrylamide, as well as those in which the anion of the above-described compounds is substituted with a sulfonate, alkyl sulfonate, acetate or alkyl carboxylate.

[0035] Specific examples thereof include monomethyl diallyl ammonium chloride, trimethyl-2-(methacryloyloxy)ethyl ammonium chloride, triethyl-2-(methacryloyloxy)ethyl ammonium chloride, trimethyl-2-(acryloyloxy)ethyl ammonium chloride, triethyl-2-(acryloyloxy)ethyl ammonium chloride, trimethyl-3-(methacryloyloxy)propyl ammonium chloride, triethyl-3-(methacryloyloxy)propyl ammonium chloride, trimethyl-2-(methacryloylamino)ethyl ammonium chloride, triethyl-2-(methacryloylamino)ethyl ammonium chloride, trimethyl-2-(acryloylamino)ethyl ammonium chloride, triethyl-

2-(acryloylamino)ethyl ammonium chloride, trimethyl-3-(methacryloylamino)propyl ammonium chloride, triethyl-3-(methacryloylamino)propyl ammonium chloride, trimethyl-3-(acryloylamino)propyl ammonium chloride, triethyl-3-(acryloylamino)propyl ammonium chloride, N,N-dimethyl-N-ethyl-2-(methacryloyloxy)ethyl ammonium chloride, N,N-diethyl-N-methyl-2-(methacryloyloxy)ethyl ammonium chloride, N,N-dimethyl-N-ethyl-3-(acryloylamino)propyl ammonium chloride, trimethyl-2-(methacryloyloxy)ethyl ammonium bromide, trimethyl-3-(acryloylamino)propyl ammonium bromide, trimethyl-2-(methacryloyloxy)ethyl ammonium sulfonate, and trimethyl-3-(acryloylamino)propyl ammonium acetate.

[0036] Examples of the other copolymerizable monomers include N-vinylimidazole, and N-vinyl-2-methylimidazole.

[0037] The non-mordant monomers refer to monomers not containing a basic or cationic moiety such as primary to tertiary amine groups and salts thereof and quaternary ammonium bases and not interacting or substantially not interacting with a dye in ink-jet ink.

[0038] Examples of the non-mordant monomers include, for example, alkyl (meth)acrylates; cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate; aryl (meth)acrylates such as phenyl (meth)acrylate; aralkyl esters such as benzyl (meth)acrylate; aromatic vinyl compounds such as styrene, vinyltoluene and α -methylstyrene; vinyl esters such as vinyl acetate, vinyl propionate and vinyl versatate; allyl esters such as allyl acetate; halogen-containing monomers such as vinylidene chloride and vinyl chloride; vinyl cyanides such as (meth)acrylonitrile; and olefins such as ethylene and propylene.

[0039] The alkyl (meth)acrylates are preferably alkyl (meth)acrylates whose alkyl moiety has 1 to 18 carbon atoms, and examples thereof include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, and stearyl (meth)acrylate.

[0040] Among these compounds, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate and hydroxyethyl methacrylate are preferable.

[0041] The non-mordant monomers can also be used alone or in combination thereof.

[0042] In addition, preferable examples of the polymer mordants include polydiallyldimethyl ammonium chloride, polymethacryloyloxyethyl- β -hydroxyethyl dimethyl ammonium chloride, polyethylenimine, polyamide-polyamine resin, cationic starch, dicyandiamide-formalin condensates, dimethyl-2-hydroxypropyl ammonium salt polymers, and polyamidine.

Hydrophobic organic acid

[0043] A hydrophobic organic acid containing 4 or more carbon atoms and an ammonium salt of the hydrophobic organic acid, in addition to the diallyldimethyl cation polymer described above, are preferably incorporated in the invention from the viewpoint of prevention of coloration (file yellowing) with time. The number of carbon atoms in the hydrophobic organic acid is preferably 4 or more, and more preferably 5 or more. The hydrophobic organic acid may be a polyvalent acid or polymer acid, and the valence of the acid is not limited. The content of the hydrophobic organic acid is varied depending on the type of acid, and the content is regulated preferably to attain a suitable pH value of the film.

[0044] Examples of the hydrophobic organic acid include those having an acidic group such as carboxyl group, sulfo group ($-\text{SO}_3\text{H}$) and phosphono group ($-\text{PO}(\text{OH})_2$), and sulfonic acid is particularly preferable. The hydrophobic organic acid may have two or more acidic groups in one molecule. Preferable examples of the hydrophobic organic acid include toluenesulfonic acid, benzenesulfonic acid, benzoic acid, naphthalenesulfonic acid, naphthalenedisulfonic acid, naphthalenetrisulfonic acid, propargylic acid, styrenesulfonic acid, 2-ethylhexanoic acid and cyclohexylcarboxylic acid, and ammonium salts thereof are also preferable. Toluenesulfonic acid and ammonium styrenesulfonate are particularly preferable.

[0045] The total content of the hydrophobic organic acids (ammonium salts) containing 4 or more carbon atoms is preferably 50 to 200 parts by mass, and more preferably 60 to 180 parts by mass, relative to 100 parts by mass of the organic mordant. When the total content is 50 parts by mass or more, file yellowing can be more sufficiently prevented, and when the total content is 200 parts by mass or less, blurring with time can be prevented, and deterioration of ink absorption can be prevented.

Fine inorganic particles

[0046] The ink-jet recording sheet of the invention preferably contains fine inorganic particles such as silica produced by a gas phase method, fine hydrous silica particles, colloidal silica, titanium dioxide, barium sulfate, calcium silicate, zeolite, kaolinite, halloysite, mica, talc, calcium carbonate, magnesium carbonate, calcium sulfate, boehmite and pseudo-boehmite, and among these compounds silica produced by a gas phase method is particularly preferable.

[0047] Only one kind of fine inorganic particles may be used, or two or more kinds of fine inorganic particles may be

used in combination. When the silica produced by a gas phase method is used in combination with other fine inorganic particles, the content of the silica produced by a gas phase method in the whole of the fine inorganic particles is preferably at least 90% by mass, and more preferably at least 95% by mass.

[0048] Usually, fine silica particles are divided roughly into particles produced by a wet method and particles produced by a dry method (gas phase method), depending on their production method. A process of decomposing silicates with an acid to form active silica and then suitably polymerizing the silica to aggregate and precipitate it and to give hydrous silica is mainly used as the wet method. On the other hand, the gas phase method used is mainly a process of hydrolyzing silicon halides in a high-temperature gaseous phase (flame hydrolysis) or a process of heating, reducing and gasifying silica sand and cokes by an arc in an electric furnace and oxidizing them with the air (arc method) to give anhydrous silica, and the "silica produced by a gas phase method" refers to fine anhydrous silica particles obtained by the gas phase method.

[0049] The silica produced by a gas phase method is different from the hydrous silica in respect of the density of surface silanol groups and the presence of voids to show different properties, and is suitable for formation of a three-dimensional structure having a high percentage of void. The reason for this is not evident, but it is estimated that the density of silanol groups on the surfaces of the fine hydrous silica particles is as high as 5 to 8 groups/nm², and then the fine silica particles easily densely aggregate, while the density of silanol groups on the surfaces of fine particles of the silica produced by a gas phase method is as low as 2 to 3 groups/nm² and the particles form loose soft flocculates having a structure of high percentage of void.

[0050] The silica produced by a gas phase method is characterized by having a large specific surface area and high absorption and retention of ink and low refractive index. So when dispersed to a suitable particle diameter, the silica can give transparency to the accepting layer to achieve high color density and excellent color formation. From the viewpoint of achieving high color density and good coloring gloss, it is important for the accepting layer to be transparent in order to apply it not only to an overhead projector (OHP) requiring transparency but also to recording sheets such as photo glossy paper.

[0051] The average primary particle diameter of the silica produced by a gas phase method is preferably 30 nm or less, more preferably 20 nm or less, still more preferably 10 nm or less, and most preferably 3 to 10 nm. Since particles of the silica produced by a gas phase method easily adhere to one another via hydrogen bonds of silanol groups, the silica particles having the average primary particle diameter of 30 nm or less can form a structure having a high percentage of void to effectively improve ink absorption properties.

Water-soluble resin

[0052] The ink-jet recording sheet of the invention preferably contains as a water-soluble resin polyvinyl alcohol, polyvinyl acetal, cellulose resin [e.g. methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), and carboxymethyl cellulose (CMC)], chitins, chitosans, starch; resins having an ether linkage, such as polyethylene oxide (PEO), polypropylene oxide (PPO), polyethylene glycol (PEG) and polyvinyl ether (PVE); and resins having an amide group or amide linkage, such as polyacrylamide (PAAM) and polyvinyl pyrrolidone (PVP), as well as resins containing a carboxyl group as the dissociable group, such as polyacrylates, maleic acid resin, alginates, gelatin, and among them polyvinyl alcohol is particularly preferably contained.

[0053] The water-soluble resins may be used alone or in combination thereof. When the polyvinyl alcohol is used in combination with the other water-soluble resins, the content of the polyvinyl alcohol in the whole of the water-soluble resins is preferably 90% by mass or more, and more preferably 95% by mass or more.

[0054] Examples of the polyvinyl alcohol include polyvinyl alcohol (PVA), cation-modified polyvinyl alcohol, anion-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol and polyvinyl alcohol derivatives. These polyvinyl alcohols may be used alone or in combination thereof.

[0055] The PVA has a hydroxyl group in its structural unit, and the hydroxyl group forms a hydrogen bond with a silanol group on the surfaces of the fine silica particles, thus facilitating formation of a three-dimensional network structure having secondary particles of the fine silica particles as a chain unit. It is estimated that by formation of this three-dimensional network structure, the colorant-accepting porous layer having a high percentage of void can be formed.

[0056] In ink-jet recording, the colorant-accepting porous layer obtained in the manner described above can absorb ink rapidly by capillary action to form excellent circular dots without ink blurring.

[0057] When the content of polyvinyl alcohol is too low, film strength may lower and the film may crack at the time of drying. Moreover, the content of polyvinyl alcohol is too high, voids are easily clogged with a resin and then percentage of void lowers to reduce ink absorption. In order to avoid such situations, the content of the polyvinyl alcohol is preferably 9 to 40% by mass, and more preferably 16 to 33% by mass with respect to the total solid content of the colorant-accepting layer.

[0058] From the viewpoint of preventing cracking, the polyvinyl alcohol described above has a number average polymerization degree of 1,800 or more, and more preferably 2,000 or more. From the viewpoint of transparency and

the viscosity of a coating solution for the colorant-accepting layer, PVA having a saponification degree of 90% or more is preferable, and PVA having a saponification degree of 95% or more is particularly preferable.

-Ratio of silica produced by a gas phase method to polyvinyl alcohol-

[0059] The ratio of silica produced by a gas phase method (i) (or the whole of fine inorganic particles when used in combination with other fine inorganic particles) to polyvinyl alcohol (p) (or the whole of water-soluble resins when used in combination with other water-soluble resins) [PB ratio (i:p), that is, the ratio of the weight of silica produced by a gas phase method to 1 part by mass of polyvinyl alcohol] significantly affects the film structure of the colorant-accepting layer. That is, when the PB ratio is increased, the percentage of void, the volume of pores and the surface area (per unit mass) are increased.

[0060] Specifically, the PB ratio (i:p) is preferably from 1.5:1 to 10:1 in order to prevent problems due to a too high PB ratio, for example a reduction in film strength and cracking at the time of drying, and to prevent problems due to a too low PB ratio, for example easy clogging of the voids with a resin, reduction in percentage of void and then the reduction in ink absorption.

[0061] When the recording sheet is passing through a transfer system in an ink-jet printer, it may be subject to stress. Therefore the colorant-accepting layer should have sufficient film strength. To prevent cracking, and peeling-off of the colorant-accepting layer when the recording material is cut into sheets, the colorant-accepting layer should also have sufficient film strength.

[0062] In this case, the PB ratio is preferably from 5:1 or less and, from the viewpoint of securing high-sprdd(rapid) ink absorption in an ink-jet printer, is preferably 2:1 or more.

[0063] For example, when a coating solution in which the fine anhydrous silica particles with an average primary diameter of 20 nm or less and the water-soluble resin have been dispersed in a PB ratio of from 2:1 to 5:1 in an aqueous solution is applied onto a substrate and the coating layer is dried, a three-dimensional network structure having secondary particles of the fine silica particles as a chain unit is formed, and a light-transmittable porous film having an average pore diameter of 30 nm or less, a percentage of void of 50 to 80%, a specific pore volume of at least 0.5 ml/g and a specific surface area of at least 100 m²/g can be easily formed.

Cross-linking agent

[0064] Preferably, the ink-jet recording sheet of the invention further contains a cross-linking agent capable of cross-linking the water-soluble resin in the coating layer (porous layer) containing the fine inorganic particles (silica produced by a gas phase method) and the water-soluble resin (PVA).

[0065] The cross-linking agent capable of cross-linking the water-soluble resin may be selected suitably in consideration of relation with the water-soluble resin used in the colorant-accepting layer, and in particular, boron compounds are preferable from the viewpoint of rapid cross-linking reaction, and examples of the boron compounds include, for example, borax, boric acid, borates (for example, orthoborates, InBO₃, ScBO₃, YBO₃, LaBO₃, Mg₃(BO₃)₂, and Co₃(BO₃)₂), diborates (for example, Mg₂B₂O₅, and CO₂B₂O₅), metaborates (for example, LiBO₂, Ca(BO₂)₂, NaBO₂, and KBO₂), tetraborates (for example, Na₂B₄O₇·10H₂O), and pentaborates (for example, KB₅O₈·4H₂O, Ca₂B₆O₁₁·7H₂O, and CsB₅O₅). Among these compounds, borax, boric acid and borates are preferable from the viewpoint of rapid cross-linking reaction, and borates are more preferable.

[0066] Further, glyoxal, melamine-formaldehyde (for example, methylol melamine, and alkylated methylol melamine), methylol urea, resol resin, polyisocyanate, and epoxy resin can also be used.

[0067] For example, when gelatin is used in combination with the above-mentioned polyvinyl alcohol, the cross-linking agent used can be compounds known as gelatin hardeners, such as, aldehyde compounds such as formaldehyde, glyoxal and glutaraldehyde; ketone compounds such as diacetyl and cyclopentanediol; active halogen compounds such as bis(2-chloroethyl urea)-2-hydroxy-4,6-dichloro-1,3,5-triazine and 2,4-dichloro-6-S-triazine sodium salt; active vinyl compounds such as divinylsulfonic acid, 1,3-vinylsulfonyl-2-propanol, N,N'-ethylene-bis(vinylsulfonylaceta-mide) and 1,3,5-triacryloyl-hexahydro-S-triazine; N-methylol compounds such as dimethylol urea and methylol dimethyl hydantoin; isocyanate compounds such as 1,6-hexamethylene diisocyanate; aziridine compounds described in USP Nos. 3,017,280 and 2,983,611; carboxyimide compounds described in USP No. 3,100,704; epoxy compounds such as glycerol triglycidyl ether; ethyleneimino compounds such as 1,6-hexamethylene-N,N'-bis-ethylene urea; and halogenated carboxyaldehyde compounds such as mucochloric acid and mucophenoxychloric acid; dioxane compounds such as 2,3-dihydroxydioxane; and chromium alum, potassium alum, zirconium sulfate and chromium acetate.

[0068] These cross-linking agents may be used alone or in combination thereof.

[0069] When the colorant-accepting layer in the ink-jet recording sheet is prepared from first and second coating solutions, the cross-linking agent may be contained in either the first or second coating solution.

[0070] The content of the cross-linking agent is preferably 2 to 40% by mass, and more preferably 3 to 30% by mass,

relative to the water-soluble resin.

[0071] The first and second coating solutions will be described later.

Surfactant

[0072] The ink-jet recoding sheet of the invention preferably contains a surfactant. When the first and second coating solutions are used to prepare the colorant-accepting layer in the ink-jet recording sheet, it is preferable that the first coating solution contains a nonionic or amphoteric surfactant while the second coating solution contains a nonionic surfactant.

[0073] Examples of the nonionic surfactant include polyoxyalkylene alkyl ethers and polyoxyalkylene alkyl phenyl ethers (for example, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, and polyoxyethylene nonyl phenyl ether), oxyethylene-oxypropylene block copolymers, esters of sorbitan and a fatty acid (for example, sorbitan monolaurate, sorbitan monooleate, and sorbitan trioleate), esters of polyoxyethylene sorbitan and a fatty acid (for example, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monooleate, and polyoxyethylene sorbitan trioleate), esters of polyoxyethylene sorbitol and a fatty acid (for example, polyoxyethylene sorbitol tetraoleate), esters of glycerin and a fatty acid (for example, glycerol monooleate), esters of polyoxyethylene glycerin and a fatty acid (polyoxyethylene glycerin monostearate, and polyoxyethylene glycerin monooleate), esters of polyoxyethylene and a fatty acid (polyethylene glycol monolaurate, and polyethylene glycol monooleate) and polyoxyethylene alkyl amines, and among them polyoxyalkylene alkyl ethers are preferable. The nonionic surfactant can be used in both the first and second coating solutions. The above nonionic surfactants may be used alone or in combination thereof. The nonionic surfactant when used in both the first and second coating solutions may be the same or different.

[0074] Examples of the amphoteric surfactant include those of amino acid type, carboxy ammonium betaine type, sulfone ammonium betaine type, ammonium sulfate betaine type and imidazolium betaine type, and for example, surfactants described in USP No. 3,843,368, JP-A Nos. 59-49535, 63-236546, 5-303205, 8-262742 and 10-282619 can be preferably used. The amphoteric surfactant is preferably an amino acid-type amphoteric surfactant, and as described in JP-A No. 5-303205, the amino acid-type amphoteric surfactant is a derivative of an amino acid (glycine, glutamic acid, and histidine), and examples thereof include N-aminoacyl acids into which a long-chain acyl group has been introduced, as well as salts thereof. These amphoteric surfactants can be used alone, in combination thereof, or in combination with the nonionic surfactant.

[0075] The content of the nonionic or amphoteric surfactant in the first coating solution is preferably 0.01 to 1%, and particularly preferably 0.03 to 0.6%. The content of the nonionic surfactant in the second coating solution is preferably 0.001 to 0.5%, and particularly preferably 0.05 to 0.3%.

Organic solvent with a high boiling point

[0076] By containing the nonionic or amphoteric surfactant and an organic solvent with a high boiling point in the first coating solution, curling of the ink-jet recording sheet can be prevented.

[0077] The organic solvent with a high boiling point is preferably the water-soluble one, and examples of the water-soluble organic solvent with a high boiling point include alcohols such as, for example, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, glycerin, diethylene glycol monobutyl ether (DEGMBE), triethylene glycol monobutyl ether, glycerin monomethyl ether, 1,2,3-butanetriol, 1,2,4-butanetriol, 1,2,4-pentanetriol, 1,2,6-hexanetriol, thiodiglycol, triethanolamine and polyethylene glycol (with a weight average molecular weight of 400 or less), and diethylene glycol monobutyl ether (DEGMBE) is preferable.

[0078] The content of the organic solvent having a high boiling point in the first coating solution is preferably 0.05 to 1%, and particularly preferably 0.1 to 0.6%.

Ozone discoloration inhibitor

[0079] The ink-jet recording sheet of the invention can include an ozone discoloration inhibitor such as thiourea or thiocyanate to prevent ozone discoloration.

[0080] The thiourea can be guanyl thiourea.

[0081] Examples of the thiocyanate include, for example, ammonium thiocyanate, zinc thiocyanate, calcium thiocyanate, potassium thiocyanate, sodium thiocyanate, magnesium thiocyanate, aluminum thiocyanate, lithium thiocyanate, silver thiocyanate, chloromethyl thiocyanate, cobalt thiocyanate, copper thiocyanate, lead thiocyanate, barium thiocyanate, and benzyl thiocyanate. The thiourea and thiocyanate may be used alone or in combination thereof.

[0082] In the invention, the thiourea or thiocyanate may be added to either of the first or second coating solution, but for stability of the solution, it is preferably added to the second coating solution and applied onto the colorant-accepting

layer. The content of the thiourea or thiocyanate in the colorant-accepting layer is preferably 1 to 20% by mass, and particularly preferably 2 to 10% by mass. When the content is less than 1% by mass, its effect on prevention of ozone discoloration is hardly exhibited, while when the content is higher than 20% by mass, cracking may occur.

5 Other components

[0083] The ink-jet recording sheet of the invention may contain the following components if necessary.

[0084] For the purpose of preventing deterioration of the colorant, discoloration inhibitors such as various UV absorbents, antioxidants, singlet oxygen quenchers may be contained.

10 **[0085]** The UV absorbents can be cinnamic acid derivatives, benzophenone derivatives, and benzotriazolylphenol derivatives. Examples thereof include butyl α -cyano-phenylcinnamate, o-benzotriazole phenol, o-benzotriazole-p-chlorophenol, o-benzotriazole-2,4-di-t-butylphenol, and o-benzotriazole-2,4-di-t-octyl phenol. Hindered phenol compounds can also be used as UV absorbents, and phenol derivatives substituted with a branched alkyl group at at least one of the 2- and 6-positions.

15 **[0086]** Benzotriazole UV absorbents, salicylic acid UV absorbents, cyanoacrylate UV absorbents, and oxalic acid anilide UV absorbents can also be used. These absorbents are described in JP-A Nos. 47-10537, JP-A 58-111942, 58-212844, 59-19945, 59-46646, 59-109055, 63-53544, Japanese Patent Application Publication (JP-B) Nos. 36-10466, 42-26187, 48-30492, 48-31255, 48-41572, 48-54965, 50-10726, and USP Nos. 2,719,086, 3,707,375, 3,754,919 and 4,220,711.

20 **[0087]** Fluorescent whitening agent can also be used as UV absorbents and can be for example coumarin fluorescent whitening agents. Specifically, they are described in JP-B Nos. 45-4699, and 54-5324.

[0088] Examples of the antioxidants include those described in European Patent Laid-Open Nos. 223,739, 309,401, 309,402, 310,551, 310,552 and 459,416, German Patent Laid-Open No. 3,435,443, JP-A Nos. 54-48535, 60-107384, 60-107383, 60-125470, 60-125471, 60-125472, 60-287485, 60-287486, 60-287487, 60-287488, 61-160287, 25 61-185483, 61-211079, 62-146678, 62-146680, 62-146679, 62-282885, 62-262047, 63-051174, 63-89877, 63-88380, 63-88381, 63-113536, 63-163351, 63-203372, 63-224989, 63-251282, 63-267594, 63-182484, 1-239282, 2-262654, 2-71262, 3-121449, 4-291685, 4-291684, 5-61166, 5-119449, 5-188687, 5-188686, 5-110490, 5-1108437, 5-170361, and JP-B Nos. 48-43295, 48-33212, and USP Nos. 4,814,262, and 4,980,275.

30 **[0089]** Specific examples of, the antioxidants include 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-1-phenyl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, 6-ethoxy-1-octyl-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline, nickel cyclohexanoate, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-2-ethylhexane, 2-methyl-4-methoxy-diphenylamine, and 1-methyl-2-phenylindole.

[0090] The discoloration inhibitors described above may be used alone or in combination thereof. The discoloration inhibitor may be rendered water-soluble, or dispersed or emulsified, or contained in microcapsules.

35 **[0091]** The amount of the discoloration inhibitor added is preferably 0.01 to 10% by mass of the colorant-accepting layer coating solution.

[0092] For the purpose of improving the dispersibility of the fine inorganic particles, the coating solution may contain any inorganic salt and a pH adjusting agent such as acid or alkali.

40 **[0093]** Further, the coating solution may contain fine particles of a metal oxide having electron conductivity for the purpose of preventing the frictional electrification or peeling electrification on the surface, or any matting agent for the purpose of reducing frictional properties on the surface.

<Method of forming the colorant-accepting layer>

45 **[0094]** Preferably, the ink-jet recording sheet of the invention contains the colorant-accepting layer on the surface of a substrate.

[0095] The colorant-accepting layer is a layer prepared by applying a first coating solution containing the fine inorganic particles with an average primary particle diameter of 20 nm or less, the water-soluble resin, the diallyldimethyl cation polymer and the cross-linking agent capable of cross-linking the water-soluble resin, followed by cross-linking and curing the coating layer, and the cross-linking and curing is preferably conducted by applying a second coating solution containing at least one selected from the polyallyl amine and polyvinyl amine and at least one selected from the hydrophobic organic acid containing 4 or more carbon atoms and an ammonium salt of the hydrophobic organic acid, onto the coating layer or film, (1) when the first coating solution is applied, (2) while the coating layer formed by applying the first coating solution is dried and before the coating layer's drying rate lespes, or (3) after the coating layer 55 formed by applying the first coating solution is dried to form a film.

[0096] In the ink-jet recording sheet produced in the manner described above, at least one (mordant) selected from polyamine and polyvinylamine is separately (contained in the second coating solution and) applied whereby the water resistance of the colorant-accepting layer can be improved. That is, when the mordant is added to the coating solution

for the colorant-accepting layer, the cationic mordant may aggregate in the coexistence of silica produced by a gas phase method and having an anionic charge thereon, but when the second coating solution containing the mordant and the coating solution (first coating solution) for the colorant-accepting layer are prepared independently and applied separately, the mordant can be selected from a broader range of mordants without considering aggregation of the fine inorganic particles.

[0097] Further, the ink-jet recording sheet produced in the manner described above can effectively prevent cracking during drying of the coating layer. That is, when the first coating solution is applied or before the coating layer's drying rate lapses, the second coating solution penetrates into the coating layer and reacts rapidly with polyvinyl alcohol in the coating layer, thus gelling (curing) the polyvinyl alcohol to improve the film strength of the coating layer instantly and significantly.

[0098] In the invention, the first coating solution containing silica produced by a gas phase method, a diallyldimethyl cation polymer, PVA, a cross-linking agent, a nonionic or amphoteric surfactant and an organic solvent with a high boiling point can be prepared for example in the following manner.

[0099] That is, the silica produced by a gas phase method is added to water, and the cationic resin is further added thereto and dispersed with an high-pressure homogenizer, a sand mill or the like, followed by adding the cross-linking agent. Thereafter, an aqueous solution of polyvinyl alcohol is added thereto (such that the amount of PVA is for example about 1/3 relative to the silica produced by a gas phase method), and further the nonionic or amphoteric surfactant and the organic solvent with a high boiling point are added thereto and stirred to prepare the first coating solution. The resultant coating solution is a uniform sol, and applied to a substrate by a coating method described later, whereby the colorant-accepting porous layer having a three-dimensional network structure can be obtained.

[0100] The cross-linking agent is added before addition of polyvinyl alcohol (water-soluble resin) (that is, the polyvinyl alcohol is added to the diluted cross-linking agent), whereby the polyvinyl alcohol can be partially cross-linked and cracking of the surface of the resultant sheet can be prevented.

[0101] The pH value of the first coating solution in the ink-jet recording sheet produced as described above is preferably 5 or less, more preferably 4.2 or less, and still more preferably 3.7 or less. When the pH value of the first coating solution is 5 or less, the print density, sharpness and glossiness of images can be effectively improved. The pH value of the first coating solution can be adjusted to 5 or less by suitably selecting the type and amount of the cationic resin added. Further, an inorganic acid or an alkali may be added for adjustment.

[0102] Further, a pH adjusting agent, and an antistatic agent can be added to the first coating solution (coating solution for the colorant-accepting layer) if necessary.

[0103] Application of the first coating solution (coating solution for the colorant-accepting layer) can be carried out by a known coating means such as an extrusion die coater, an air doctor coater, a blade coater, a rod coater, a knife coater, a squeeze coater, a reverse roll coater, and a bar coater.

[0104] After application of the first coating solution, the coating layer is coated with the second coating solution, and the second coating solution is applied more preferably before the coating layer's drying rate lapses.

[0105] The pH value of the second coating solution is preferably 8.5 or more, more preferably 9.0 or more, and still more preferably 9.2 or more. When the pH value of the second coating solution is 8.5 or more, cracking of the colorant-accepting layer can be improved more sufficiently.

[0106] The phrase "before the coating layer's drying rate lapses" refers, usually, to several minutes just after application of the colorant-accepting layer coating solution, during which the coating layer shows a constant drying rate, that is, the content of the solvent in the applied coating solution is reduced in proportion to time. The time when such a constant drying rate appears is described in Kagaku Kogaku Binran (Chemical Engineering Handbook), pp. 707 to 712 published on October 25, 1980 by Maruzen Co., Ltd.

[0107] After application of the first coating solution, the coating layer is dried until the coating layer's drying rate lapses, as described above, and this drying is conducted generally at 50 to 180°C for 0.5 to 10 minutes (preferably 0.5 to 5 minutes). The drying time, though being varied depending on the amount of the coating, is preferably in the range described above.

[0108] Example of the method of applying the second coating solution before the above coating layer's drying rate lapses include (1) a method of further applying the second coating solution onto the coating layer, (2) a method of spraying the second solution with a spray, and (3) a method of dipping a substrate having the coating layer formed thereon into the second coating solution.

[0109] In the method (1) described above, application of the second coating solution can be carried out by a known coating means such as a curtain flow coater, an extrusion die coater, an air doctor coater, a blade coater, a rod coater, a knife coater, a squeeze coater, a reverse roll coater and a bar coater. However, a method of using an extrusion die coater, a curtain flow coater or a bar coater is preferably used since these coaters are not directly contacted with the previously formed coating layer.

[0110] The amount of the first coating solution added to the substrate is preferably 150 to 250 g/m², and more preferably 160 to 220 g/m².

[0111] The amount of the second coating solution added to the coating layer is preferably 5 to 40 g/m², and more preferably 10 to 30 g/m².

[0112] After application of the second coating solution, the coating layer is dried and cured generally by heating the layer at 40 to 180°C for 0.5 to 30 minutes. The coating layer is heated particularly preferably at 40 to 150°C for 1 to 20 minutes.

[0113] Alternatively, the second coating solution may be added simultaneously with application of the first coating solution.

[0114] In this case, the first and second coating solutions can be simultaneously applied onto a substrate such that the first coating solution is contacted with the substrate (applied in a layered form), and then dried and cured to form the colorant-accepting layer.

[0115] The simultaneous application (application in a layered form) can be carried out by a coating method using an extrusion die coater or a curtain flow coater. After simultaneous application, the formed coating layer is dried, and this drying is carried out generally by heating the coating layer at 40 to 150°C for 0.5 to 10 minutes, and preferably at 40 to 100°C for 0.5 to 5 minutes.

[0116] For example, when borax or boric acid is used as the cross-linking agent to be contained in the cross-linking solution, heating at 60 to 100°C for 5 to 20 minutes is preferable.

[0117] When the simultaneous application (application in a layered form) described above is carried out for example with an extrusion die coater, the two simultaneously jetted coating solutions are in a layered form in the vicinity of a discharge orifice of the extrusion die coater (that is, superposed layers are formed before they are disposed on a substrate), and applied in the layered form on the substrate. The superposed layers made from the coating solutions and formed before application are liable to cause cross-linking reaction at the interface between the two solutions during their being disposed on the substrate. Therefore in the vicinity of the discharge orifice of the extrusion die coater, the two discharged solutions are mixed and thickened easily, which may cause a hindrance in the coating procedure. Accordingly, when the simultaneous application is carried out as described above, a barrier layer solution (interlayer solution) composed of a material not reacting with the cross-linking agent is preferably interposed between the first and second solutions to apply the three layers simultaneously.

[0118] The barrier layer solution is not limited insofar as it can form a liquid film without reacting with the cross-linking agent. Examples thereof include water or an aqueous solution containing a very small amount of a water-soluble resin not reacting with a boron compound. The water-soluble resin should be used after consideration of coating properties as a thickening agent etc., and examples thereof include polymers such as hydroxypropylmethyl cellulose, methyl cellulose, hydroxyethylmethyl cellulose, polyvinyl pyrrolidone and gelatin.

[0119] The barrier layer solution can also contain the mordant.

[0120] As the solvent in each of the coating solutions, it is possible to use water, an organic solvent or a mixed solvent thereof. Example of the organic solvent used in the coating solution include alcohols such as methanol, ethanol, n-propanol, isopropanol and methoxypropanol, ketones such as acetone and methyl ethyl ketone, and tetrahydrofuran, acetonitrile, ethyl acetate and toluene.

[0121] After the colorant-accepting layer is formed on the substrate, the colorant-accepting layer is calendered for example by passing it through a roll nip in a supercalender or a gloss calender under heating and pressure, whereby surface smoothness, glossiness, transparency and coating strength can be improved. However, calendering can cause a reduction in percentage of void (that is, ink absorption can be lowered) and should thus be carried out under such conditions that the percentage of void is hardly reduced.

[0122] The temperature of the rolls during calendering is preferably 30 to 150°C, and more preferably 40 to 100°C.

[0123] The linear pressure between the rolls during calendering is preferably 50 to 400 kg/cm, and more preferably 100 to 200 kg/cm.

[0124] In the case of ink-jet recording, the colorant-accepting layer should have an absorption capacity enough to absorb the whole of droplets, and thus the thickness of the layer should be determined in relationship with the percentage of void in the layer. For example, when the volume of ink is 8 nL/mm² and the percentage of void is 60%, a layer having a thickness of about 15 μm or more is necessary.

[0125] In this respect, the thickness of the colorant-accepting layer is preferably 10 to 50 μm in the case of ink-jet recording.

[0126] The median diameter of pores in the colorant-accepting layer is preferably 0.005 to 0.030 μm, and more preferably 0.01 to 0.025 μm.

[0127] The percentage of void and the median pore diameter can be measured by a mercury porosimeter (Poresizer 9320-PC2 produced by Shimadzu Corporation).

[0128] The colorant-accepting layer is preferably excellent in transparency, and for this transparency, the haze of the colorant-accepting layer when formed on a transparent film substrate is preferably 30% or less, and more preferably 20% or less.

[0129] The haze can be measured with a haze meter (HGM-2DP, Suga Test Instrument Co. Ltd.).

<Substrate>

[0130] As the substrate, both a transparent substrate made of a transparent material such as plastics and an opaque substrate made of an opaque material such as paper can be used. A transparent substrate or a highly glossy opaque substrate is used preferably in order to sufficiently utilize the transparency of the colorant-accepting layer.

[0131] The material which can be used in the transparent substrate is preferably a material which is transparent and endurable against radiation heat when used in OHP or backlight displays. Examples thereof include polyesters such as polyethylene terephthalate (PET); and polysulfone, polyphenylene oxide, polyimide, polycarbonate, and polyamide. In particular, polyesters are preferable, and polyethylene terephthalate is particularly preferable.

[0132] The thickness of the transparent substrate is not particularly limited, but is preferably 50 to 200 μm from the viewpoint of handling.

[0133] The highly glossy opaque substrate is preferably the one whose surface has 40% or more glossiness at the side on which the colorant-accepting layer is disposed. The glossiness is a value determined according to a method described in JIS P-8142 (test method for 75° mirror surface glossiness of paper and plate paper). Specific examples of the highly glossy opaque substrate include highly glossy paper substrates such as art paper, coated paper, cast-coated paper, and baryta paper used for a substrate for silver salt photograph; highly glossy films (which may be subjected to surface calendering) made opaque by adding a white pigment to plastic films made of polyesters such as polyethylene terephthalate (PET), cellulose esters such as nitrocellulose, cellulose acetate and cellulose acetate butyrate, polysulfone, polyphenylene oxide, polyimide, polycarbonate and polyamide; and substrates provided with a polyolefin coating layer containing or not containing a white pigment on the surface of the above paper substrates, transparent substrates, or highly glossy film containing a white pigment.

[0134] Further, white pigment-containing foamed polyester films (for example, foamed PET containing fine polyolefin particles and having voids formed by drawing) can be used.

[0135] The thickness of the opaque substrate is not particularly limited either, but is preferably 50 to 300 μm from the viewpoint of handling.

[0136] The substrate may have been subjected to corona discharge treatment, glow discharge treatment, flame treatment, and UV irradiation treatment.

[0137] The base paper used in the paper substrate is now described in detail.

[0138] The base paper is produced from wood pulp as the main material, and, if necessary, synthetic pulp such as polypropylene or synthetic fibers such as nylon or polyester. Any of LBKP, LBSP, NBKP, NBSP, LDP, NDP, LUKP and NUKP can be used as the wood pulp, but LBKP, NBSP, LBSP, NDP and LDP containing a large amount of short fibers are used preferably in a large amount.

[0139] The proportion of LBSP and/or LDP is preferably 10 to 70% by mass.

[0140] Chemical pulp (sulfate pulp and sulfite pulp) including less impurity is preferably used as the pulp, and pulp whose whiteness has been improved by bleaching is also useful.

[0141] A sizing agent such as higher fatty acids and alkyl ketene dimers, a white pigment such as calcium carbonate, talc and titanium oxide, a wet and dry strength agent such as starch, polyacrylamide and polyvinyl alcohol, a fluorescent whitening agent, a water holding agent such as polyethylene glycol, a dispersant, and a softener such as quaternary ammonium can be added to the base paper, if necessary.

[0142] The freeness of the pulp used in paper manufacturing is preferably 200 to 500 ml according to provisions of CSF, and the fiber length after beating is preferably 30 to 70% in terms of % by mass of 24- and 42-mesh residues in total as prescribed in JIS P-8207. The amount of 4-Mesh residues is preferably 20% by mass or less.

[0143] The weight of the base paper is preferably 30 to 250 g, and particularly preferably 50 to 200 g. The thickness of the base paper is preferably 40 to 250 μm . The base paper can be endowed with high smoothness by calendering it during or after paper manufacturing. The density of the base paper is generally 0.7 to 1.2 g/m^2 (JIS P-8118).

[0144] Further, the rigidity of the base paper is preferably 20 to 200 g under the conditions prescribed in JIS P-8143.

[0145] The surface of the base paper may be coated with a surface sizing agent, and the usable surface sizing agent is the one that can be added to the above-described base paper.

[0146] The pH value of the base paper, when measured by a hot water extraction method prescribed in JIS P-8113, is preferably 5 to 9.

[0147] The polyethylene with which the obverse and reverse of the base paper are coated is mainly low-density polyethylene (LDPE) and/or high-density polyethylene (HDPE), but LLDPE and, or polypropylene can also be used therewith.

[0148] In particular, the polyethylene layer at the side where the colorant-accepting layer is to be formed is preferably the one whose opaqueness and whiteness have been improved by adding rutile or anatase type titanium oxide to polyethylene as is widely conducted for photographic paper. The content of titanium oxide is preferably about 3 to 20% by mass, and more preferably 4 to 13% by mass, relative to the polyethylene.

[0149] The polyethylene coating paper can be used not only as glossy paper but also as paper having a matted

surface or a silk-like surface which ordinary photographic paper has by embossing it upon melt-extruding polyethylene onto the surface of the base paper.

EXAMPLES

[0150] Hereinafter, the present invention is described in more detail by reference to the Examples, but the invention is not limited to the Examples. In the Examples, the terms "parts" and "%" refer to "parts by mass" and "% by mass" respectively unless otherwise specified, and the number following "WM" indicates "weight average molecular weight", and the terms "polymerization degree" refer to "weight average polymerization degree".

-Preparation of substrate-

[0151] Wood pulp composed of 100 parts of LBKP was beaten with a double disk refiner to the Canadian freeness of 300 ml, and 0.5 part of epoxylated behenic amide, 1.0 part of anion polyacrylamide, 0.1 part of polyamide polyamine epichlorohydrin and 0.5 part of cation polyacrylamide, all of which are expressed in terms of the ratio thereof based on a bone dry weight basis with respect to the pulp, were added to the pulp and the resultant mixture was weighed with a Fourdrinier paper machine to prepare a paper of 170 g/m².

[0152] To regulate surface sizing of the base paper, the base paper was impregnated, in an amount of 0.5 g/m² on a bone dry weight basis, with 4% aqueous solution containing polyvinyl alcohol and 0.04% of fluorescent whitening agent (Whitex BB, Sumitomo Chemical Co., Ltd.), dried, and calendered and a base paper whose density was regulated to be 1.05 was obtained.

[0153] The wire surface (reverse) of the resultant base paper was subjected to corona discharge treatment and then coated with high-density polyethylene by a melt extrusion machine so that the thickness of the polyethylene became 19 μm, to form a resin layer having a matted surface (hereinafter, the surface of the resin layer is referred to as "reverse"). The resin layer at the side of this reverse was further subjected to corona discharge treatment and then coated, in an amount of 0.2 g/m² on a bone dry weight basis, with a dispersion in which aluminum oxide (Alumina Sol 100, Nissan Chemical Industries, Ltd.) and silicon dioxide (Snowtex O, Nissan Chemical Industries, Ltd.) were dispersed as an antistatic agent in the ratio of 1:2 (ratio by weight) in water.

[0154] Further, the felt surface (obverse) of the base paper was subjected to corona discharge treatment, and then low-density polyethylene having a MRF (melt flow rate) of 3.8, containing 10% of anatase type titanium oxide, a trace of ultramarine and 0.01% of fluorescent whitening agent (relative to polyethylene) was melt-extruded onto the felt surface so that the thickness thereof became 29 μm, to form a highly gloss thermoplastic resin layer on the obverse of the base paper (hereinafter, this highly glossy surface is referred to as "obverse"), whereby a substrate was prepared.

Example 1

-Preparation of first coating solution-

[0155] (1) In the composition described below, fine silica particles produced by a gas phase method were mixed with (2) deionized water, and (3) dimethyldiallyl ammonium chloride was mixed therewith, and the mixture was dispersed by a Dynomill KDP (Sinmal Enterprises Ltd.) and then (4) a 8% aqueous solution of polyvinyl alcohol and (5) an aqueous solution of boric acid were added thereto while the mixture was stirred, and further (6) polyoxyethylene lauryl ether and (7) diethylene glycol monobutyl ether were added thereto to prepare a first coating solution having pH of 3.3.

Composition of the first coating solution

[0156]

- | | |
|---|------------|
| (1) Fine silica particles produced by a gas phase method (fine inorganic particles) | 16 parts |
| (QS-30 with a specific surface area of 300 m ² /g by BET method, produced by Tokuyaka Corp.) | |
| (2) Deionized water | 107 parts |
| (3) Polydimethyldiallyl ammonium chloride | 1.7 parts |
| (PAS-H-5L, WM : 40,000, solids content : 28%, produced by Nittobo K.K.) | |
| (4) 8% aqueous solution of polyvinyl alcohol (water-soluble resin) | 44.3 parts |
| (PVA 124, degree of saponification : 98.5%, degree of polymerization : 2400, produced by Kuraray Co., Ltd.) | |
| (5) Boric acid | 0.65 part |
| (6) Polyoxyethylene lauryl ether (surfactant) | 0.19 part |
| (Emulgen 109P (10%), Kao Corporation) | |

(7) Diethylene glycol monobutyl ether (DEGMBE) 0.58 part

-Preparation of ink-jet recording sheet-

[0157] After the obverse of the substrate was subjected to corona discharge treatment, the first coating solution obtained above was applied in an amount of 200 ml/m² onto the obverse of the substrate by an extrusion die coater (coating step), and dried at 80°C with a hot-air dryer (wind velocity : 3 to 8 m/sec) until the solids content of the coating layer was reduced to 20%. The coating layer indicated a constant drying rate during this period. Just thereafter, the substrate was dipped in a second coating solution having the following composition for 30 seconds, to permit the coating solution to adhere in an amount of 20 g/m² to the coating layer, and then dried at 80°C for 10 minutes (drying step). A colorant-accepting layer having a thickness after drying of 32 μm was thus formed on the substrate to prepare the ink-jet recording sheet (1) of the invention.

Composition of the second coating solution

[0158]

- Deionized water 76 parts
- 10% aqueous solution of polyallylamine (PAA10-C, WM : 15,000, Nittobo K.K.) 27 parts
- Polyoxyethylene lauryl ether (surfactant) (Emulgen 109P (10%), Kao Corporation) 2.0 parts
- Toluenesulfonic acid 3 parts

Example 2

[0159] The ink-jet recording sheet (2) of the invention was prepared in the same manner as in Example 1 except that the composition of the second coating solution was changed to the following composition.

Composition of the second coating solution

[0160]

- Deionized water 76 parts
- 10% aqueous solution of polyallylamine (PAA10-C, WM : 15,000, Nittobo K.K.) 27 parts
- Polyoxyethylene lauryl ether (surfactant) (Emulgen 109P (10%), Kao Corporation) 1 part
- Ammonium toluenesulfonate 3 parts

Example 3

[0161] The ink-jet recording sheet (3) of the invention was prepared in the same manner as in Example 1 except that the composition of the second coating solution was changed to the following composition.

Composition of the second coating solution

[0162]

- Deionized water 76 parts
- 10% aqueous solution of polyallylamine (PAA10-C, WM : 15,000, Nittobo K.K.) 27 parts
- Polyoxyethylene lauryl ether (surfactant) (Emulgen 109P (10%), Kao Corporation) 1 part
- 2-Ethylhexanoic acid 3 parts

Example 4

[0163] The ink-jet recording sheet (4) of the invention was prepared in the same manner as in Example 1 except that the composition of the first coating solution was changed to the following composition.

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Composition of the first coating solution (pH = 3.3)

[0164]

- 5 (1) Fine silica particles produced by a gas phase method (fine inorganic particles) 16 parts
(QS-30, specific surface area 300 m²/g by BET method, produced by Tokuyaka Corp.)
(2) Deionized water 107.8 parts
(3) Polydimethyldiallyl ammonium chloride 0.9 part
(Sharol DC902P, WM : 9,000, solids content : 51%, produced by Dai-ichi Kogyo Seiyaku Co., Ltd.)
10 (4) 8% aqueous solution of polyvinyl alcohol (water-soluble resin) 44.3 parts
(PVA 124, degree of saponification : 98.5%, degree of polymerization : 2400, produced by Kuraray)
(5) Boric acid 0.65 part
(6) Polyoxyethylene lauryl ether (surfactant) 0.19 part
(Emulgen 109P (10%), Kao Corporation)
15 (7) Diethylene glycol monobutyl ether (DEGMBE) 0.58 part

Comparative Example 1

- 20 [0165] The comparative ink-jet recording sheet (1) was prepared in the same manner as in Example 1 except that the composition of the second coating solution was changed to the following composition.

Composition of the second coating solution

[0166]

- 25 - Deionized water 87 parts
- Ammonia water (10%) 20 parts
- Polyoxyethylene lauryl ether (surfactant) 1 part
(Emulgen 109P (10%), Kao Corporation)
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Comparative Example 2

- 35 [0167] The comparative ink-jet recording sheet (2) was prepared in the same manner as in Example 1 except that the composition of the first coating solution was changed to the following composition.

Composition of the first coating solution (pH = 3.3)

[0168]

- 40 (1) Fine silica particles produced by a gas phase method (fine inorganic particles) 16 parts
(QS-30, specific surface area 300 m²/g by BET method, produced by Tokuyaka Corp.)
(2) Deionized water 103.5 parts
(3) Polyamidine 5.2 parts
(SC700 Kai, WM : 6,000, solids content : 30%, produced by HYMO Co., Ltd.)
45 (4) 8% aqueous solution of polyvinyl alcohol (water-soluble resin) 44.3 parts
(PVA 124, degree of saponification : 98.5%, degree of polymerization : 2400, produced by Kuraray)
(5) Boric acid 0.65 part
(6) Polyoxyethylene lauryl ether (surfactant) 0.19 part
(Emulgen 109P (10%), Kao Corporation)
50 (7) Diethylene glycol monobutyl ether (DEGMBE) 0.58 part

<Performance Evaluation>

- 55 [0169] The ink-jet recording sheets (1) to (4) of the invention and the comparative ink-jet recording sheets (1) to (2) obtained above were evaluated as follows. The evaluation results are shown in Table 1.

Rate of absorption of ink

[0170] An ink-jet printer (PM-900C, Seiko Epson Corporation) was used to make solid images of yellow (Y), magenta (M), cyan (C), black (K), blue (B), green (G) and red (R) on the colorant-accepting layer of each recording sheet, and thereafter (10 seconds later), a paper was contacted with and pushed against the images, and depending on the degree of transfer of the ink to the paper, the rate of absorption of the ink was evaluated according to the following criteria.

[Criteria]

[0171]

AA: No transfer of the ink onto the paper was recognized (indicating a good ink absorption rate).

CC: Partial transfer of the ink onto the paper was recognized.

Water resistance

[0172] In the same manner as described above in evaluation of the rate of absorption of ink, solid images of yellow (Y), magenta (M), cyan (C), black (K), blue (B), green (G) and red (R) were printed, then allowed to stand for 3 hours and dipped in water for 1 minute, and the degree of elution of the ink into water was evaluated with naked eyes according to the following criteria.

[Criteria]

[0173]

AA: No elution of the dyes was recognized.

BB: Partial elution of the dyes was recognized to cause partial reduction in the color density of the images.

CC: The dyes were completely eluted into water.

Blurring with time

[0174] Line patterns (line width 0.28 mm) having a magenta ink and a black ink alternately arranged in a checkered form were printed on each of the ink-jet recording sheets by the same printer as used in measurement of ink absorption rate, and the visual density was measured with X-Rite 310TR (X-Rite, Incorporated). After printing, each sheet was allowed to stand for 3 hours and then stored for 1 day in an air-conditioned chamber at 40°C under 90% relative humidity, and the visual density was measured again, and blurring with time was evaluated according to the difference in density (ΔOD). A lower density difference (ΔOD) indicates that blurring with time was suppressed.

Glossiness

[0175] The 60° glossiness of the surface of the colorant-accepting layer in each recording sheet before printing was measured by a digital angle-varied glossmeter (UGV-50DP, manufactured by Suga Test Instrument Co. Ltd.).

Print density

[0176] An ink-jet printer (PM-900C, Seiko Epson Corporation) was used to print solids images of yellow (Y), magenta (M), cyan (C), black (K), blue (B), green (G) and red (R) on each ink-jet recording sheet, and the density of the K (black) portion was measured by an X-Rite densitometer.

File yellowing

[0177] The resultant recording sheet was placed in a plastic file (CLEAR BOOK, produced by Kokuyo Co., Ltd.) such that the sheet partially stuck out from the file, and then was allowed to stand in a room for 1 month, then the recording sheet was removed, and the portions of the sheet inside and outside the file were measured for their Y (yellow) density by an X-Rite densitometer. Yellowing can be expressed in terms of difference in Y (ΔOD_Y) between the portions of the sheet inside and outside the file. A lower difference in Y indicates less yellowing, and ○ was given to a sheet indicating ΔOD_Y of 0.02 or less.

Table 1

	Ink Absorption Rate	Water Resistance	Blurring with Time	Glossiness (%)	Density of Black	File Yellowing
Example 1	AA	AA	0.24	52	2.32	○
Example 2	AA	AA	0.26	55	2.31	○
Example 3	AA	AA	0.30	53	2.33	○
Example 4	AA	AA	0.20	51	2.28	○
Comparative Example 1	AA	AA	0.56	28	2.16	○
Comparative Example 2	AA	AA	0.41	38	2.07	○

[0178] As is evident from Table 1, the ink-jet recording sheets (1) to (4) of the invention were superior in ink absorption rate, water resistance and blurring with time and had high glossiness and print density, and file yellowing did not occur.

[0179] On the other hand, the comparative ink-jet recording sheets (1) to (2) were inferior in blurring with time and glossiness.

Claims

1. An ink-jet recording sheet comprising a diallyldimethyl cation polymer and at least one selected from a polyallyl amine and a polyvinyl amine.
2. The ink-jet recording sheet of claim 1, further comprising a least one selected from the group consisting of a hydrophobic organic acid containing 4 or more carbon atoms and an ammonium salt of the hydrophobic organic acid.
3. The ink-jet recording sheet of claim 1 or 2, further comprising fine inorganic particles and a water-soluble resin.
4. The ink-jet recording sheet of any one of the claims 1 to 3, further comprising a cross-linking agent capable of cross-linking the water-soluble resin.
5. An ink-jet recording sheet having a colorant-accepting layer on a surface of a substrate, wherein the colorant-accepting layer is a layer prepared by applying a first coating solution containing fine inorganic particles with an average primary particle diameter of 20 nm or less, a water-soluble resin, a diallyldimethyl cation polymer and a cross-linking agent capable of cross-linking the water-soluble resin, followed by cross-linking and curing the coating layer, the cross-linking and curing being conducted by applying a second coating solution containing at least one selected from polyallyl amine and polyvinyl amine and at least one selected from a hydrophobic organic acid containing 4 or more carbon atoms and an ammonium salt of the hydrophobic organic acid, onto the coating layer or film, (1) when the first coating solution is applied, (2) while the coating layer formed by applying the first coating solution is dried and before the coating layer's drying rate lapses, or (3) after the coating layer formed by applying the first coating solution is dried to form a film.
6. The ink-jet recording sheet of claim 5, wherein the colorant-accepting layer has a three-dimensional network structure with a void percentage of 50 to 80%, and the ratio of the fine inorganic particles to the water-soluble resin by mass is 1.5 to 10.
7. The ink-jet recording sheet of any one of the claims 1 to 6, wherein the cross-linking agent is a boron compound.
8. The ink-jet recording sheet of any one of the claims 3 to 7, wherein the fine inorganic particles are silica produced by a gas phase method.

9. The ink-jet recording sheet of any one of the claims 2 to 8, wherein the hydrophobic organic acid is a sulfonic acid having an aromatic ring.

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