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(54) METHOD FOR PRODUCING INKJET RECORDING MATERIAL

(57) Provided is a method for producing an inkjet recording material, the method comprising the steps of mixing an aqueous solution of a saponified vinyl acetate-diacetone acrylamide copolymer with a crosslinking agent to give a liquid mixture (a) ; adding a water-soluble basic compound to the liquid mixture (a) after a lapse of at least 30 minutes to give another liquid mixture (b); and mixing the obtained liquid mixture (b) with porous inorganic fine particles to give an ink receiving layer coating liquid and applying the coating liquid to a support, the inkjet recording material being characterized in that the ink receiving layer comprises the porous inorganic fine particles, the saponified vinyl acetate-diacetone acrylamide copolymer, and the crosslinking agent.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing an inkjet recording material, in particular a method for producing an inkjet recording material which has an excellent water resistance and is also resistant to cracking that may occur during production.

BACKGROUND ART

[0002] Inkjet recording system is a method in which droplets of ink sprayed from a nozzle are fixed on the surface of a recording medium for recording of text, images, etc. This system has many advantages, such as easy color printing, low running cost, and low noise level, and therefore is widely used in home and office printers. In recent years, along with the spread of digital cameras, the recording system has been accepted as an alternative to silver halide photography. In addition, various inkjet recording materials (including optical disks, such as CD, DVD, and BD, on whose surfaces direct printing can be performed) are selected depending on the purpose, and the inkjet recording materials are thus desired to have higher quality and a wider range of variety.

[0003] An inkjet recording material has an ink receiving layer formed on a support which is a paper sheet, a plastic sheet, a plastics disk, etc. In the ink receiving layer, a hydrophilic resin binder is used to bind a porous inorganic material, such as silica and alumina. The porous inorganic material rapidly absorbs ink, prevents ink from bleeding, and thereby serves for the formation of appropriate dots with a perfectly round shape, which enables expression of fine images. The binder resin is required to have (1) a high affinity for ink, (2) a strong force for binding porous inorganic particles, etc., and widely used as the binder resin is, for example, polyvinyl alcohol (hereinafter abbreviated as PVA) resin etc.

[0004] In recent years, inkjet recording system is required to have high expressiveness, that is, high definition, and improved printing speed. The approach that has been taken to achieve high definition is to increase the amount of discharged ink per unit area of the recording material, and for that reason recording materials are required to be capable of absorbing more ink as compared to conventional recording materials. Therefore, the ink receiving layer needs to have higher porosity, and the development thereof is aimed at reducing the amount of the binder resin.

[0005] Regarding improvement in printing speed, higher printing speed increases the physical load on the surface of the recording material being conveyed in a printer, and the absorption of a large amount of ink as mentioned above results in increase in the load on the recording material in a wet state. Therefore, in addition to the above (1) and (2), the binder resin should have properties such as (3) a binding force strong enough to prevent, even when the amount of the binder resin added to a coating liquid is small, cracking on the surface of the ink receiving layer during drying of the coating liquid, (4) a high viscosity in a state of an aqueous solution as a coating liquid so as not to permeate porous fine particles but to secure high porosity of the inorganic particles, (5) a high water resistance so as to achieve a high surface strength even in a wet state, etc.

[0006] Patent Literature 1 discloses a technique in which PVA having a polymerization degree of 4000 or higher is used as the binder contained in the ink receiving layer of the inkjet recording material. Such a highly polymerized PVA has a strong binding force and an aqueous solution thereof has a high viscosity. Therefore, even when only a small amount of the binder is used, cracking at the time of drying is less likely to occur, and high porosity of the fine particles can be secured.

[0007] However, the above- mentioned PVA lacks a sufficient surface strength in a wet state, a sufficient binding force, and a sufficient aqueous solution viscosity. In addition, such a highly polymerized PVA has a problem of extremely low production efficiency. As for industrially produced PVAs, the upper limit of the polymerization degree is about 4500. To produce a PVA having a higher polymerization degree, special equipment or a production method sacrificing the productivity (with less yield) is required, leading to extremely high cost, which becomes an industrial disadvantage.

[0008] Meanwhile, a technique using PVA and a boron compound is disclosed (for example, Patent Literature 2 and Patent Literature 3) . In this technique, boric acid and/or borax used as a crosslinking agent increases the viscosity of an aqueous solution of PVA, prevents the binder resin from permeating the porous inorganic fine particles, and thus secures high porosity of the inorganic particles. In this way, the boric acid and/or borax contributes to improvement of the binding force and of the surface strength in a wet state, even when used in a small amount.

[0009] Recently, however, reproductive toxicity of boron compounds, such as boric acid, has been pointed out, and the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) has included the compounds in the candidate list of Substance of Very High Concern (SVHC) . These situations have made it difficult to use boron compounds, and therefore a PVA resin binder having a crosslinking system as an alternative to the PVA/ boron compound is desired.

[0010] To solve these problems, the present inventors proposed an inkjet recording material using a saponified diacetone acrylamide-fatty acid vinyl ester copolymer and a hydrazine compound (Patent Literature 4). In addition, Patent Literature 5 proposed an inkjet recording material comprising a PVA resin having an acetoacetic ester group, and a multivalent hydrazide compound.

[0011] A binder obtainable by allowing such a PVA resin having a keto group to react with such a hydrazine compound as a crosslinking agent can be used to produce an inkjet recording material which has an excellent water resistance and a high surface strength in a wet state. However, due to the low viscosity of the aqueous solution of the binder, the solution permeates the porous inorganic fine particles and prevents the large amount of ink from being sufficiently absorbed. This insufficient ink absorption results in low definition of images, and therefore an improved binder is desired. In addition, since the binder resin partially permeates the pores in the fine particles, the amount of the binder used to bind the particles is reduced. Thus, the problem of cracking at the time of drying has not been completely solved.

[0012] The use of a modified PVA resin and a crosslinking agent as a binder involves a problem of pot life. Since the crosslinking reaction of the modified PVA resin with the crosslinking agent proceeds even in an aqueous solution, the aqueous solution containing the mixture of the two becomes thicker over time. In a system formed of a PVA resin having an acetoacetic ester group and a multivalent hydrazide compound, the reaction rate is especially high, and the coating liquid for the ink receiving layer unfavorably turns into a gel in the middle of coating.

[0013] A system formed of a saponified diacetone acrylamide-fatty acid vinyl ester copolymer and a hydrazine compound also has a similar problem, but the problem of pot life can be solved by the method that the present inventors proposed (Patent Literature 6), in which a diacetone acrylamide copolymer-modified PVA, a water-soluble hydrazine compound, and a water-soluble organic amine or ammonia coexist. As described in paragraph [0022] of Patent Literature 6, in this method, available work time is prolonged by adding beforehand a water-soluble organic amine or ammonia to an aqueous solution of a diacetone acrylamide copolymer-modified PVA and subsequently adding a water-soluble hydrazine compound to suppress the rapid reaction between the diacetone acrylamide copolymer-modified PVA and the hydrazine compound.

[0014] However, when porous inorganic fine particles are mixed with the liquid mixture obtained by this method, that is, a liquid mixture of a saponified diacetone acrylamide- fatty acid vinyl ester copolymer, a hydrazine compound, and a water- soluble organic amine or ammonia, due to the low viscosity of the liquid mixture, the binder resin and the crosslinking agent permeate the pores in the fine particles, which reduces the amount of the binder used for binding the particles and the ink absorbability.

CITATION LIST

[Patent Literature]

[0015]

- [PTL 1] JP 07-117334 A
- [PTL 2] JP 11-20306 A
- [PTL 3] JP 11-192777 A
- [PTL 4] JP 11-348417 A
- [PTL 5] JP 2001-213045 A
- [PTL 6] JP 10-87936 A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0016] An object of the present invention is to provide a method for stably producing an inkjet recording material on which fine images can be expressed even in high-speed printing (for example, at a speed of 10 ppm (page per minute) or higher). More specifically, an object of the present invention is to provide a method for producing an inkjet recording material characterized in that a PVA resin composition which is highly water resistant and exhibits a strong binding force even when added in a small amount is used as a binder, that the viscosity of an aqueous solution of the binder is high at the time of mixing with porous inorganic fine particles, and that the viscosity of a coating liquid obtained by the mixing does not significantly change.

SOLUTION TO PROBLEM

[0017] The present inventors made extensive investigation and found that the problems described above can be solved at once by a method for producing an inkjet recording material having an ink receiving layer on a support, the ink receiving layer comprising porous inorganic fine particles, a saponified vinyl acetate-diacetone acrylamide copolymer, and a crosslinking agent, the method comprising mixing an aqueous solution of the saponified vinyl acetate-diacetone acrylamide copolymer with the crosslinking agent, adding a water-soluble basic compound to the mixture after a lapse of at least 30 minutes, mixing the obtained liquid mixture with the porous inorganic fine particles to give an ink receiving layer coating liquid, and applying the coating liquid to a support. The present inventors conducted further examination and completed the present invention.

[0018] That is, the present invention relates to the following.

[1] A method for producing an inkjet recording material, the method comprising the steps of mixing an aqueous solution of a saponified vinyl acetate-diacetone acrylamide copolymer with a crosslinking agent to give a liquid mixture (a); adding a water-soluble basic compound to the liquid mixture (a) after a lapse of at least 30 minutes to give another liquid mixture (b); and mixing the obtained liquid mixture (b) with porous inorganic fine particles to give an ink receiving layer coating liquid and applying the coating liquid to a support, the inkjet recording material being characterized in that the ink receiving layer comprises the porous inorganic fine particles, the saponified vinyl acetate-diacetone acrylamide copolymer, and the crosslinking agent.

[2] A method for producing an inkjet recording material, the method comprising the steps of mixing an aqueous solution of a saponified vinyl acetate-diacetone acrylamide copolymer with a crosslinking agent to give a liquid mixture (a); after the liquid mixture (a) has thickened, adding a water-soluble basic compound to the liquid mixture (a) and mixing them to give another liquid mixture (b); and mixing the obtained liquid mixture (b) with porous inorganic fine particles to give an ink receiving layer coating liquid and applying the coating liquid to a support, the inkjet recording material being characterized in that the ink receiving layer comprises the porous inorganic fine particles, the saponified vinyl acetate-diacetone acrylamide copolymer, and the crosslinking agent, and that the ratio of (B) the viscosity of the liquid mixture (b) immediately after the mixing with the water-soluble basic compound to (A) the viscosity of the liquid mixture (a) immediately after the mixing with the crosslinking agent [(B)/(A)] is 1.5 to 10.0.

[3] The method of the above [1] or [2], wherein the crosslinking agent is a compound having 2 or more functional groups selected from the group consisting of hydrazino, hydrazide, and semicarbazide.

[4] The method of any one of the above [1] to [3], wherein the water-soluble basic compound is one or more selected from the group consisting of ammonia and a water-soluble organic amine.

[5] The method of any one of the above [1] to [4], wherein the viscosity of a 4% by weight aqueous solution of the saponified vinyl acetate-diacetone acrylamide copolymer measured by the method of JIS K-6726 (1994) is 10 to 100 mPa·s.

ADVANTAGEOUS EFFECTS OF INVENTION

[0019] The method for producing an inkjet recording material of the present invention is highly productive and industrially advantageous because the viscosity of the coating liquid for preparing an ink receiving layer has an excellent stability, and cracking on the surface of the ink receiving layer does not occur during drying process. In addition, the inkjet recording material produced by the method of the present invention is excellent in ink absorbability, surface strength, and water resistance, and therefore can produce fine images even in high-speed printing (for example, at a speed of 10 ppm (page per minute) or higher). Furthermore, the present invention does not use any boron compounds, and therefore is free from problems of reproductive toxicity, etc. and thus highly safe.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

Fig. 1 shows measured results of the time-dependent change in the viscosity of liquid mixtures containing 8% by weight of the saponified vinyl acetate-diacetone acrylamide copolymer (DAVES) of Synthetic Example 1 described later and 0.4% by weight of adipic acid dihydrazide (ADH) with or without 0.1% by weight of isopropanolamine (IPAm).

DESCRIPTION OF EMBODIMENTS

[0021] Hereinafter, the method for producing an inkjet recording material of the present invention will be described in detail.

[0022] The saponified vinyl acetate-diacetone acrylamide copolymer (hereinafter abbreviated as DAVES) used in the present invention can be produced by a publicly known method, such as copolymerization of vinyl acetate and diacetone acrylamide followed by saponification of the obtained copolymer.

[0023] The method for copolymerization of vinyl acetate and diacetone acrylamide may be any publicly known polymerization method, such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization, etc. Inter alia, solution polymerization with the use of methanol as the solvent is industrially preferable.

[0024] The method for saponification of the polymer obtained by copolymerization of vinyl acetate and diacetone acrylamide may be any publicly known alkaline saponification or acid saponification. Inter alia, a method involving alcoholysis, in which an alkali hydroxide is added to a solution of the polymer in methanol or in a liquid mixture of methanol and water, methyl acetate, benzene, or the like, is industrially preferable.

[0025] As long as the effects of the present invention are not hindered, the above DAVES may be copolymerized with one or more kinds selected from olefins, such as ethylene, propylene, isobutylene, α- octene, and α- dodecen; vinylene carbonates; unsaturated acids, such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, and undecylenic acid, salts thereof, or mono- or di- alkyl esters thereof; nitriles, such as acrylonitrile and methacrylonitrile; amides, such as acrylamide and methacrylamide; olefin sulfonic acids, such as vinylsulfonic acid, allylsulfonic acid, and methallyl sulfonic acid, or salts thereof; alkyl vinyl ethers; vinyl esters, such as vinyl formate, vinyl propionate, and vinyl butyrate; N- acrylamidemethyltrimethylammonium chloride, allyltrimethylammonium chloride, dimethyldiallylammonium chloride, dimethylallyl vinyl ketone, N- vinyl pyrrolidone, vinyl chloride, vinylidene chloride; polyoxyalkylene (meth) allyl ethers, such as polyoxyethylene (meth) allyl ether, and polyoxypropylene (meth) allyl ether; polyoxyalkylene (meth) acrylates, such as polyoxyethylene (meth) acrylate and polyoxypropylene (meth) acrylate; polyoxyalkylene (meth) acrylamides, such as polyoxyethylene (meth) acrylamide and polyoxypropylene (meth) acrylamide; polyoxyethylene (1- (meth) acrylamide- 1, 1- dimethylpropyl) ester, polyoxyethylene vinyl ether, polyoxypropylene vinyl ether, polyoxyethylene allylamine, polyoxypropylene allylamine, polyoxyethylene vinylamine, polyoxypropylene vinylamine, isopropenyl acetate, vinyl ethylene carbonate, 2, 2- dialkyl- 4- vinyl- 1, 3- dioxolane, glycerin monoallyl ether 3, 4- diacetoxy- 1- butene, 1, 4- diacetoxy- 2- butene, etc., which can copolymerize with vinyl acetate or diacetone acrylamide. In addition, as long as the effects of the present invention are not hindered, the obtained DAVES may be subjected to post modification by reactions, such as acetalization, urethanation, etherification, grafting, phosphorylation, acetoacetylation, cationization, etc.

[0026] The content of the diacetone acrylamide unit in the above DAVES is not particularly limited, but preferably in the range of 0.5 to 15 mol%, and more preferably in the range of 1 to 10 mol%. A lower content of the diacetone acrylamide unit may cause reduction in water resistance or moisture resistance, and a higher content may make it impossible to prepare the aqueous coating liquid due to reduction in water solubility.

[0027] The saponification degree of the above DAVES is not particularly limited, but the saponification degree measured by the method of JIS K-6726 (1994) is preferably 80 mol% or higher, and more preferably 85 mol% or higher.

[0028] The polymerization degree of the above DAVES is not particularly limited, but preferably 4500 or lower for improved industrial productivity. Regarding the viscosity of the DAVES, the viscosity of a 4% by weight aqueous solution measured by the method of JIS K-6726 (1994) (rotational viscometer method) is preferably 10 to 100 mPa·s, and more preferably 20 to 80 mPa·s.

[0029] The crosslinking agent used in the present invention is not particularly limited unless it hinders the effects of the present invention, and preferred examples include compounds having 2 or more functional groups of one or more kinds selected from the group consisting of hydrazino represented by the following formula (1) :

$$-NH-NH_2 \qquad (1),$$

hydrazide represented by the following formula (2) :

$$-CO-NH-NH_2 \qquad (2),$$

and semicarbazide represented by the following formula (3) :

$$-NH-CO-NH-NH_2 \qquad (3),$$

each of which has reactivity with the ketone groups of the DAVES.

[0030] Specific examples of the crosslinking agent include multifunctional hydrazine and hydrazide compounds, such as carbohydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, suberic acid dihydrazide, azelaic acid dihydrazide, sebacic acid dihydrazide, dodecanediohydrazide, hexadecanediohydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 2, 6- naphthoic acid dihydrazide, 4, 4'- bis (benzenedihydrazide), 1, 4- cyclohexanedihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, itaconic acid dihydrazide, ethylenediaminetetraacetic acid tetrahydrazide, citric acid trihydrazide, butanetricarbohydrazide, 1, 2, 3- benzene trihydrazide, 1, 4, 5, 8- naphthoic acid tetrahydrazide, nitriloacetic acid trihydrazide, cyclohexanetricarboxylic acid trihydrazide, pyromellitic acid tetrahydrazide, and N- amino polyacrylamide; and semicarbazide compounds, such as N, N'- hexamethylene bissemicarbazide, and biuretly- tri (hexamethylene- N, N'- dimethylsemicarbazide) . The examples also include multifunctional hydrazine derivatives, multifunctional hydrazide derivatives, and multifunctional semicarbazide derivatives obtained by reactions between these compounds and low boiling point ketones, such as acetone and methylethylketone.

[0031] The amount of the above-mentioned crosslinking agent is not particularly limited, but preferably 1 to 20 parts by weight, more preferably 2 to 15 parts by weight, and further preferably 3 to 10 parts by weight relative to 100 parts by weight of DAVES. Too low amount of the crosslinking agent reduces not only the water resistance and moisture resistance but also the viscosity of the liquid mixture containing DAVES and the crosslinking agent at the time of mixing with the porous inorganic fine particles, resulting in impaired porosity of the fine particles. On the other hand, too high amount of crosslinking agent makes the viscosity of the coating liquid unstable, thus reduces productivity, and also causes the migration of the crosslinking agent not involved in the reaction and as a result reduces water resistance. In the present invention, DAVES and the crosslinking agent are used as a binder.

[0032] Examples of the method for mixing DAVES and the crosslinking agent in the present invention include a method in which an aqueous solution of the crosslinking agent is added to and mixed with an aqueous solution of DAVES prepared beforehand. The temperature at the time of mixing DAVES and the crosslinking agent is not particularly limited, and is usually about 10 to 60°C. The aqueous solution of DAVES can be prepared by a conventionally known method for dissolving PVA resin, that is, a method including dispersing a DAVES resin in water at room temperature, raising the temperature of the water to 80°C or higher with stirring, and, after complete dissolution, cooling the solution. For mixing DAVES and the crosslinking agent, it is allowable that a solid crosslinking agent is added to an aqueous solution of DAVES. However, for more homogenous reaction, it is preferable that an aqueous solution of the crosslinking agent prepared beforehand is added to an aqueous solution of DAVES.

[0033] The water-soluble basic compound used in the present invention will be described. In the present invention, considering that the viscosity of the liquid mixture of DAVES and the crosslinking agent increases over time while the reaction of DAVES and the crosslinking agent proceeds, a water-soluble basic compound is added to prevent the viscosity increase and gelation of the coating liquid during the process of mixing the porous inorganic fine particles with the liquid mixture prepared by mixing DAVES and the crosslinking agent and during the process of applying the coating liquid onto a support. Since the rate of the reaction between DAVES and the crosslinking agent is high in acidic conditions and low in basic conditions, the water-soluble basic compound may be any compound as long as it raises the pH of the system. Inter alia, water-soluble organic amines and ammonia are preferred in that these have a strong inhibitory effect on the reaction between DAVES and the crosslinking agent and in that these volatilize during coating and drying of the coating liquid and therefore do not impair the properties and water resistance of the recording material.

[0034] In addition to water- soluble organic amines and ammonia, examples of the water- soluble basic compound include hydroxides of alkali metals, such as sodium hydroxide and potassium hydroxide; hydroxides of alkaline earth metals, such as calcium hydroxide; etc. As the water- soluble organic amine, amines that may be used are one or more kinds selected from the group consisting of primary alkanolamines, such as monoethanolamine, aminoethylethanolamine, monoisopropanolamine, N- (2- hydroxypropyl)- ethylenediamine, 2- amino- 1- butanol, 2- amino- 2- methyl-1- propanol, 3- amino- 1- propanol, 2- amino- 2- methyl- 1, 3- propanediol, 2- amino- 2- ethyl- 1, 3- propanediol, and tris (hydroxyethyl)- aminomethane; secondary alkanolamines, such as diethanolamine, methylethanolamine, butylmethanolamine, N- acetylethanolamine, and diisopropanolamine; tertiary alkanolamines, such as triethanolamine, methyldiethanolamine, dimethylethanolamine, diethylethanolamine, ethyldiethanolamine, and triisopropanolamine; primary alkylamines, such as methylamine, ethylamine, isobutylamine, tert- butylamine, and cyclohexylamine; secondary alkylamines, such as dimethylamine, diethylamine, and diisopropylamine; and tertiary alkylamines, such as trimethylamine. The amount of the water- soluble basic compound is preferably 0.05 to 20 parts by weight, and more preferably 0.1 to 10 parts by weight relative to 100 parts by weight of DAVES.

[0035] The porous inorganic fine particles used in the present invention may be, for example, white inorganic pigments or inorganic sols, such as wet synthetic silica, colloidal silica, vapor phase method silica, light calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc carbonate, satin white, aluminum silicate, diatomaceous earth, calcium silicate, magnesium silicate, tin oxide sol, cerium oxide sol, lanthanum oxide sol, titanium oxide sol, neodymium oxide sol, yttrium oxide sol, colloidal alumina, quasi-boehmite alumina, vapor phase method alumina, aluminium hydroxide, alumina, lithopone, zeolite, hydrated halloysite, magnesium carbonate, and magnesium hydroxide, and these may be used alone or in combination of two or more kinds depending on the purpose. The wet synthetic silica is further classified into precipitated silica, gel silica, and sol silica by the production method. The precipitated silica is produced by the reaction of sodium silicate and sulfuric acid in alkaline conditions. The grown silica particles from the reaction agglomerate and precipitate and are subsequently subjected to filtration, washing with water, drying, grinding, and classification to be made into a commercial product. Examples of commercially available precipitated silica include the NIPSIL (trade name) series from Tosoh Silica and the TOKSIL (trade name) series and the FINESIL (trade name) series from Tokuyama. The gel silica is produced by the reaction of sodium silicate and sulfuric acid in acidic conditions. While aging, minute particles dissolve and reprecipitate as if to bind other primary particles. As a result, recognizable primary particles disappear and relatively hard agglomerated particles having internal voids are formed. Examples of commercially available gel silica include NIPGEL (trade name) from Tosoh Silica and SYLOID and SYLOJET1 (trade name) from Grace Japan. The sol silica, which is also called colloidal silica, can be obtained by double decomposition of sodium silicate and an acid etc., or by heat aging a silica sol after passed through an ion-exchange resin layer. Examples of commercially available sol silica include SNOWTEX (trade name) from Nissan Chemical. Vapor phase method silica is also called dry method silica in comparison to wet method silica and is generally produced by flame hydrolysis. Specifically, in a generally known method, the vapor phase method silica is obtained by combustion of tetrachlorosilane with hydrogen and oxygen. However, instead of tetrachlorosilane, silanes, such as methyltrichlorosilane and trichlorosilane may be used alone or as a mixture with tetrachlorosilane. Examples of commercially available vapor phase method silica include AEROSIL from Nippon Aerosil and QS type from Tokuyama.

[0036] The particle size of the porous inorganic fine particles used in the present invention is not particularly limited as long as the effects of the present invention are not hindered, and is appropriately selected depending on the type of the inorganic fine particles to be used. For example, preferred mean particle sizes are about 1 to 12 μm in the case of wet synthetic silica, about 5 to 100 nm in the case of colloidal silica, and about 30 nm or less in the case of vapor phase method alumina and quasi-boehmite alumina. The above mean particle sizes are determined by electron microscope observation (average of Martin's diameters of particles in, for example, a 5-cm square of an electron micrograph at 10,000 to 400,000-fold magnification; see "Biryushi handbook (Handbook of Fine Particles)", Asakura Publishing, p. 52, 1991).

[0037] The ratio of the porous inorganic fine particles and DAVES to be used depends on the type of the porous inorganic fine particles and the purpose, but the weight ratio of DAVES/porous inorganic fine particles is preferably 1/100 to 100/100, and more preferably 3/100 to 50/100.

[0038] In the preparation of the ink receiving layer coating liquid containing DAVES, the crosslinking agent, the water-soluble basic compound, the porous inorganic finer particles, and water, the order and timing of mixing of these components is important. The present inventors investigated the time-dependent change in the viscosity of a liquid mixture of DAVES and the crosslinking agent, and of liquid mixtures to which the water-soluble basic compound was added at different timings. Fig. 1 shows measured results of the time-dependent change in the viscosity of the liquid mixtures containing 8% by weight of DAVES and 0.4% by weight of adipic acid dihydrazide (ADH) with or without 0.1% by weight of isopropanolamine (IPAm) at 20°C.

[0039] In Fig.1, [1] is the time-dependent change in the viscosity of the liquid mixture of DAVES and ADH without the addition of the water-soluble basic compound, which shows that immediately after the addition of ADH, the crosslinking reaction occurred and the viscosity rapidly rose. In Fig.1, [2] is the time-dependent change in the viscosity of the liquid mixture of DAVES and IPAm to which ADH was added, which shows that IPAm suppressed the crosslinking reaction between DAVES and ADH and as a result the viscosity of the liquid mixture became stable at a low level. In Fig. 1, [3] is the time-dependent change in the viscosity of the liquid mixture where IPAm was added 5 hours after the addition of ADH to DAVES. The viscosity changed in the same way as in [1] until IPAm was added and became stable thereafter.

[0040] In the preparation of the ink receiving layer coating liquid, without the addition of the basic compound, the viscosity rapidly rises as shown by [1] in Fig. 1. Such rapid rise makes it difficult to mix the porous inorganic fine particles and an aqueous solution of the binder at an appropriate viscosity. While the coating liquid is mixed or applied, the viscosity greatly changes, and in the worst case it becomes impossible to apply the coating liquid during the coating process. In cases where the cross linking agent is added to a liquid mixture of DAVES and the basic compound as shown by [2] in Fig. 1, due to the low viscosity of the aqueous solution of the binder, at the time of mixing with the porous inorganic fine particles, the binder resin and the crosslinking agent permeate the pores in the fine particles, which reduces the amount of the binder used for binding the particles and the ink absorbability.

[0041] The idea of the present invention is as follows. A crosslinking agent is added to an aqueous solution of DAVES, the liquid mixture is left stand for a predetermined period of time, and when the viscosity of the mixture reaches a desired level, a basic compound is added as in [3] in Fig. 1. By this method, the desired viscosity can be retained for a long period of time, and even after porous inorganic fine particles are mixed therewith, the permeation of the binder resin and the crosslinking agent into the pores in the fine particles can be suppressed, and the problem of thickening during the mixing and coating can also be solved.

[0042] That is, the components used for the ink receiving layer coating liquid must be mixed in the following order: an aqueous solution of DAVES and a crosslinking agent first, followed by a water-soluble basic compound, and then porous inorganic fine particles. Unless the order is followed, the effects of the present invention cannot be exerted.

[0043] In the preparation of the ink receiving layer coating liquid of the present invention, while the time from the preparation of an aqueous solution of DAVES to the addition of the crosslinking agent is not particularly limited, the timing of the addition of the water-soluble basic compound after the addition/mixing of the crosslinking agent is important. That is, the water-soluble basic compound must be added at the time when the increasing viscosity of the liquid mixture of DAVES and the crosslinking agent reaches a desired level. Since the thickening rate of the liquid mixture of DAVES and the cross linking agent varies with the concentration of the aqueous solution, the amount of the crosslinking agent, the temperature, etc., it is desirable that the right timing for adding the water-soluble basic compound (the timing at which a desired viscosity is achieved) is calculated based on the results of time-dependent change in the viscosity obtained beforehand, or is judged based on the torque and the current value of the stirrer used for stirring the liquid mixture.

[0044] The time from the obtainment of the liquid mixture (a) (as a result of mixing an aqueous solution of DAVES and the crosslinking agent) to the addition of the water-soluble basic compound depends on the concentration of the aqueous solution, the amount of the crosslinking agent, the temperature, etc. as mentioned above, and is at least 30 minutes. If the time is less than 30 minutes, the viscosity of the liquid mixture does not reach the desired level. If the desired viscosity is achieved in less than 30 minutes, the thickening rate cannot be sufficiently suppressed even after the water-soluble basic compound is added, and the viscosity may cause problems during the mixing and coating steps. As for extending the time from the obtainment of the liquid mixture (a) to the addition of the water-soluble basic compound, there is no particular limitation unless the viscosity of the liquid mixture exceeds the desired level. However, to avoid decrease in productivity due to too much extension, the time is usually 48 hours or less, preferably 12 hours or less, and more preferably 6 hours or less. To adjust the time as above, conditions, such as the concentration of the aqueous solution, the amount of the crosslinking agent, the temperature, etc. are set appropriately.

[0045] In the method of the present invention, an ink receiving layer coating liquid is prepared by mixing an aqueous solution of DAVES and a crosslinking agent to give a liquid mixture (a), and after the liquid mixture (a) has thickened, adding a water-soluble basic compound and porous inorganic fine particles are added thereto and mixed therewith. The ratio of (B) the viscosity of the liquid mixture (b) of DAVES, the crosslinking agent, and the water-soluble basic compound immediately after the addition and mixing of the water-soluble basic compound (before the addition of the porous inorganic fine particles) to (A) the viscosity of the liquid mixture (a) of DAVES and the crosslinking agent immediately after the mixing with the crosslinking agent (before the addition of the water-soluble basic compound) [(B)/(A)] is preferably 1.5 to 10.0, and more preferably 1.7 to 8.0. The viscosity ratio [(B)/(A)] of lower than 1.5 is disadvantageous because the ink absorbability of the ink receiving layer becomes low for the reason that the viscosity of the aqueous solution of the binder is too low at the time when the porous inorganic fine particles are mixed. The viscosity ratio [(B)/(A)] of higher than 10.0 is (also) disadvantageous because mixing with the porous inorganic fine particles and coating of a support become difficult for the reason that the viscosity of the aqueous solution of the binder is too high.

[0046] After the obtainment of the liquid mixture (a) as a result of mixing the aqueous solution of the DAVES and the crosslinking agent the liquid mixture (a) may be left stand or stirred until the water-soluble basic compound is added thereto. There is no particular limitation regarding the temperature, but the temperature is usually 10 to 80°C, and preferably 15 to 60°C.

[0047] The time after the obtainment of the liquid mixture (b) as a result of adding the water-soluble basic compound to the liquid mixture (a) containing DAVES and a crosslinking agent and mixing them to the addition of the porous inorganic fine particles is not particularly limited. The method for mixing the liquid mixture containing DAVES and the crosslinking agent with the porous inorganic fine particles is also not particularly limited. In order to disperse the porous inorganic fine particles as homogeneously as possible in the liquid mixture, a known mixing apparatus (e.g. high speed homogenizer etc.) or a known mixing method may be used in the preparation of the ink receiving layer coating liquid.

[0048] Unless the effects of the present invention are hindered, another water- soluble resin, a water- dispersible resin, an inorganic filler, a plasticizer, an ink fixing agent, a surfactant, etc. may be used in combination as needed. Examples of the water- soluble resin or the water- dispersible resin that can be used in combination include albumin, gelatin, casein, starch, gum arabic, cellulosic derivatives, such as methyl cellulose and hydroxyethyl cellulose; anionic water- soluble resins, such as polyamide resin, melamine resin, PVA, vinyl pyrrolidone modified PVA, N- substituted or unsubstituted (meth) acrylamide modified PVA, silanol modified PVA, sulfonic acid modified PVA, sodium poly (meth) acrylate, anion modified PVA, sodium alginate, and water- soluble polyester; cationic water- soluble resins, such as polyethyleneimine, polyvinylamine, polyallylamine, polyallylamine- sulfone copolymers and ammonium salts thereof, cationic starch, cation modified poly (meth) acrylamide, cation modified PVA, and cationic polyamide resin; and water- dispersible resins, such as SBR latex, NBR latex, vinyl acetate resin emulsion, ethylene/ vinyl acetate copolymer emulsion, (meth) acrylic ester resin emulsion, and vinyl chloride resin emulsion.

[0049] The method for producing an inkjet recording material of the present invention comprises the step of applying, to a support, the ink receiving layer coating liquid, which is obtained by the above-described method and which contains DAVES, a crosslinking agent, a water-soluble basic compound, porous inorganic fine particles, and water, thereby forming an ink receiving layer.

[0050] The materials that can be used as the support are, for example, papers including paper boards (such as Manila board, white chipboard, and liner board), printing paper (such as common wood-free paper, wood containing paper, gravure printing paper), high-grade paper, medium-grade paper, low-grade paper, news print paper, releasing paper, carbon paper, non-carbon paper, glassine paper, etc.; resin coat paper; synthetic paper; non-woven fabric; fabric; metallic foil; and films, sheets, and molds made of, thermoplastic resins including polyethylene, polypropylene, PET, polycarbonate, polyvinyl chloride, and ethylene-propylene copolymer are used.

[0051] The method for applying the coating liquid for forming the ink receiving layer on the support is not particularly limited, and a known method with the use of an air knife coater, a curtain coater, a slide lip coater, a die coater, a blade coater, a gate roll coater, a bar coater, a rod coater, a bill blade coater, a short dwell blade coater, a size press, etc., is used.

[0052] The amount of the solid content in the coating liquid is not particularly limited, and is preferably 5 to 60% by weight, more preferably 8 to 50% by weight, and further more preferably 10 to 30% by weight relative to the whole coating liquid. Too little solid content may cause not only increased drying load but also reduced uniformity in the thickness of the coating layer, and too much solid content increases the viscosity of the coating liquid, which may make it difficult to, for example, apply the coating liquid at a high speed, and therefore may decrease workability.

[0053] The method for drying the applied coating liquid on the support is not particularly limited, but in the view of productivity, the use of drying by heating, such as hot-air blowing or infrared radiation is preferred. Other drying conditions are also not particularly limited, and usually drying is performed at 90 to 120°C for about 1 to 30 minutes.

EXAMPLES

[0054] Hereinafter, the present invention will be illustrated by Examples, but it is not limited thereto. As used herein, "%" and "part" are on weight basis unless otherwise stated.

[0055] The synthesis of DAVES was performed by the method shown below. The saponification degree and the viscosity of a 4% aqueous solution of DAVES were measured according to JIS K-6726 (1994). In addition, the diacetone acrylamide content (the degree of modification) was determined by the nitrogen analysis of a sample of DAVES thoroughly washed with methanol.

[0056] Examples of the synthesis of DAVES are shown below.

<Synthetic Example 1>

[0057] Into a flask equipped with a stirrer, a thermometer, a dropping funnel, and a reflux condenser, 694 parts of vinyl acetate, 5 parts of diacetone acrylamide, and 178 parts of methanol were placed. After nitrogen replacement of the system, the internal temperature was raised to 60°C. To the system, a solution of 1 part of 2,2-azobisisobutyronitrile dissolved in 50 parts of methanol was added to start polymerization. A solution of 30 parts of diacetone acrylamide dissolved in 43 parts of methanol was added dropwise at a constant rate over 5 hours from the start of polymerization. At 6 hours from the start, m-dinitrobenzene as a polymerization inhibitor was added to stop the polymerization. The polymerization yield was 78%. The obtained reaction mixture was subjected to distillation of remaining vinyl acetate with continuous addition of methanol vapor, and thus a 50% methanol solution of a vinyl acetate polymer containing a diacetone acrylamide copolymerization component was obtained. To 500 parts of this mixture, 50 parts of methanol and 10 parts of a 4% methanol solution of sodium hydroxide were added and thoroughly mixed, and saponification was allowed to proceed at 40°C. The obtained gelatinous material was pulverized, thoroughly washed with methanol, and dried to give a saponified vinyl acetate-diacetone acrylamide copolymer. This resin was found to have a diacetone acrylamide unit content of 5. 0 mol%. The viscosity of a 4% aqueous solution of the resin at 20°C was 26.8 mPa·s and the saponification degree was 98.4 mol%.

<Synthetic Examples 2 and 3>

[0058] DAVES 2 and 3 were obtained in the same manner as in Synthetic Example 1 except that the amount of sodium hydroxide for saponification was changed and that the starting composition was changed as shown in Table 1.

[0059]

Table 1

	Resin	Starting composition (part)			Polymerization yield (%)	Analytical values for DAVES resin		
		Vinyl acetate	Methanol	Diacetone acrylamide		Degree of saponification (mol%)	Viscosity of 4% aq. soln. (mPa·s)	Degree of modification (mol%)
Syn. Ex. 1	DAVES1	694	271	35	78	98.4	26.8	5.0
Syn. Ex. 2	DAVES2	602	360	38	83	94.5	16.2	3.6
Syn. Ex. 3	DAVES3	825	150	25	58	97.6	37.9	2.5
Syn. Ex.: Synthetic Example								

<Example 1>

[0060] To 8 parts of DAVES 1 obtained in Synthetic Example 1, 92 parts of pure water was added. The mixture was heated with stirring, and after 2 hours' dissolution at 90°C, cooled to 20°C. Thus a 8% aqueous solution was obtained. To 100 parts of this aqueous solution, 4 parts of a 10% aqueous solution of adipic acid dihydrazide as a crosslinking agent was added and quickly mixed. The mixture was slowly stirred at 20°C for 4 hours, and then 0.1 part of isopropanolamine as a water-soluble basic compound was added and mixed. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 285 mPa·s, and the viscosity (B) of the aqueous solution after a lapse of 4 hours and subsequent addition and mixing of the water-soluble basic compound was 643 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
To 50 parts of the above liquid mixture, 35 parts of amorphous silica (made by Tokuyama, trade name: FINESIL X-45, mean particle size 4.5 μm) was gradually added and dispersed. To this, 5 parts of polydiallyldimethylammonium chloride (made by Nittobo, trade name: PAS-H-5L, 28% aqueous solution) as an ink fixing agent and 160 parts of pure water were added, and the mixture was stirred using a homogenizer at 5000 rpm for 10 minutes to prepare an ink receiving layer coating liquid having a solid content of 15%.
The coating liquid was applied to a wood-free paper having a basis weight of 64 g/m^2 with the use of an air knife coater so that the amount of the solid content was 13 g/m^2, and was dried at 105°C for 10 minutes to prepare an inkjet recording material.

<Example 2>

[0061] To 100 parts of an 8% aqueous solution of DAVES 1 obtained in Synthetic Example 1, which was heated to 50°C, 4 parts of a 10% aqueous solution of hexamethylenesemicarbazide (made by Asahi Kasei Chemicals, Hardener SC) as a crosslinking agent was added and quickly mixed. The mixture was slowly stirred at 50°C for 3 hours, and then 0.1 part of monoethanolamine as a water-soluble basic compound was added and mixed. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 205 mPa·s, and the viscosity (B) of the aqueous solution after 3 hours' lapse and the addition and mixing of the water-soluble basic compound was 573 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Example 3>

[0062] To 100 parts of an 8% aqueous solution of DAVES 2 obtained in Synthetic Example 2, 5 parts of a 10% aqueous solution of N-amino polyacrylamide (made by Otsuka Chemicals, APA-L) as a crosslinking agent was added and quickly mixed. The mixture was slowly stirred at 20°C for 2 hours, and then 0.2 part of ammonia as a water-soluble basic compound was added and mixed. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 87 mPa·s, and the viscosity (B) of the aqueous solution after 2 hours' lapse and the addition and mixing of the water-soluble basic compound was 518 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Example 4>

[0063] To 100 parts of an 8% aqueous solution of DAVES 3 obtained in Synthetic Example 3, 5 parts of a 10% aqueous solution of carbohydrazide as a crosslinking agent was added and quickly mixed. The mixture was slowly stirred at 20°C for 1 hour, and then 1 part of a 10% aqueous solution of sodium hydroxide as a water-soluble basic compound was added and mixed. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 758 mPa·s, and the viscosity (B) of the aqueous solution after 1 hour's lapse and the addition and mixing of the water-soluble basic compound was 1320 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Example 5>

[0064] A liquid mixture was prepared in the same manner as in Example 1 except that the time from the addition of the crosslinking agent to the addition of the water-soluble basic compound was changed from 4 hours to 6 hours. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 285 mPa·s, and the viscosity (B) of the aqueous solution after 6 hours' lapse and the addition and mixing of the water-soluble basic

compound was 1670 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Example 6>

[0065] A liquid mixture was prepared in the same manner as in Example 2 except that the time from the addition of the crosslinking agent to the addition of the water-soluble basic compound was changed from 3 hours to 40 minutes. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 205 mPa·s, and the viscosity (B) of the aqueous solution after 40 minutes' lapse and the addition and mixing of the water-soluble basic compound was 320 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Comparative Example 1>

[0066] A liquid mixture was prepared in the same manner as in Example 1 except that the time from the addition of the crosslinking agent to the addition of the water-soluble basic compound was changed from 4 hours to 15 minutes. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 285 mPa·s, and the viscosity (B) of the aqueous solution after 15 minutes' lapse and the addition and mixing of the water-soluble basic compound was 298 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Comparative Example 2>

[0067] A liquid mixture was prepared in the same manner as in Example 1 except that unmodified PVA (made by Japan VAM & POVAL, JP-18, saponification degree: 88.0 mol%, viscosity of a 4% aqueous solution: 24.1 mPa·s) was used instead of the DAVES obtained in Synthetic Example 1. The viscosity (A) of the aqueous solution immediately after the addition and mixing of the crosslinking agent was 272 mPa·s, and the viscosity (B) of the aqueous solution after 4 hours' lapse and the addition and mixing of the water-soluble basic compound was 270 mPa·s. The conditions in the preparation of the liquid mixture are shown in Table 2.
Using the above liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1.

<Comparative Example 3>

[0068] A liquid mixture was prepared in the same manner as in Example 1 except that no crosslinking agent was added, and using this liquid mixture, an inkjet recording material was prepared in the same manner as in Example 1. The conditions in the preparation of the liquid mixture are shown in Table 2.

<Comparative Example 4>

[0069] To 100 parts of an 8% aqueous solution of the DAVES obtained in Synthetic Example 1, 4 parts of a 10% aqueous solution of adipic acid dihydrazide as a crosslinking agent was added and quickly mixed. The mixture was slowly stirred at 20°C for 4 hours. No water-soluble basic compound was added to this mixture. Using this liquid mixture, an ink receiving layer coating liquid was prepared, and an attempt to apply the liquid to a wood-free paper was made. However, due to gelation of the coating liquid, the application was discontinued, and thus it was impossible to obtain an inkjet recording material. The conditions in the preparation of the liquid mixture are shown in Table 2.
[0070]

Table 2

	Resin	Crosslinking agent	Base	Left-stand temperature and time after crosslinking agent was added	(A) Viscosity before left stand [mPa·s]	(B) Viscosity after left stand [mPa·s]	(B)/(A)
Ex. 1	DAVES 1	ADH	IPAm	20°C, 4h	285	643	2.26
Ex. 2	DAVES 1	SC	MEAm	50°C, 3h	205	573	2.80

(continued)

	Resin	Crosslinking agent	Base	Left-stand temperature and time after crosslinking agent was added	(A) Viscosity before left stand [mPa·s]	(B) Viscosity after left stand [mPa·s]	(B)/(A)
Ex. 3	DAVES 2	APA	NH_3	20°C, 2h	87	518	5.95
Ex. 4	DAVES 3	CDH	NaOH	20°C, 1h	758	1320	1.74
Ex. 5	DAVES 1	ADH	IPAm	20°C, 6h	285	1670	5.86
Ex. 6	DAVES 1	SC	MEAm	50°C, 40min	205	320	1.56
Comp. Ex. 1	DAVES 1	ADH	IPAm	20°C, 15m	285	298	1.05
Comp. Ex. 2	Unmodified PVA	ADH	IPAm	20°C, 4h	272	270	0.99
Comp. Ex. 3	DAVES 1	-	IPAm	20°C, (4h)	285	285	1.00
Comp. Ex. 4	DAVES 1	ADH	-	20°C, 4h	285	-	-
Ex.: Example Comp. Ex.: Comparative Example							

In the table, ADH means adipic acid dihydrazide, SC means hexamethylene semicarbazide (Hardener SC), APA means N-amino polyacrylamide (APA-L), CDH means carbohydrazide, IPAm means isopropanolamine, and MEAm means monoethanolamine.

[0071] The inkjet recording materials of Examples and Comparative Examples prepared as above were subjected to the tests shown below. The results are shown in Table 3.

<Crack Observation>

[0072] The surface of the ink receiving layer of each inkjet recording material prepared above was observed under a 100-power microscope, and the degree of cracking was evaluated based on the following criteria.
Good: No surface cracks are observed (No problem)
Poor: Several surface cracks are observed (Unsuitable for use)
Unacceptable: Great many surface cracks are observed (Unusable)

<Surface Strength>

[0073] To the surface of the ink receiving layer of each inkjet recording material prepared above, a Mending Tape (18 mm in width) made by Sumitomo 3M was attached. After peeling off the tape, the conditions of the coating layer transferred on the tape were visually observed, and the surface strength was evaluated based on the following criteria.
Good: The coating layer was hardly transferred (No practical problem)
Poor: Part of the coating layer was transferred (Slightly problematic)
Unacceptable: Most of the coating layer was transferred (Practically problematic)

<Ink Absorbability>

[0074] The prepared inkjet recording material was set into a printer made by Seiko Epson, "PX-V630", and a black solid image was printed thereon. After the printing, the printed part of the recording sheet was rubbed with a finger at regular time intervals, and the time span before the printed part became unchanged was determined. A shorter time span means a better ink absorption rate.

<Water Resistance>

[0075] Water was applied to the printed part of the inkjet recording material, and the part was rubbed with a finger. The printed part was checked for dissolution or bleeding based on the following criteria.
Good: No bleeding was observed and the original shape was retained.
Unacceptable: Significant bleeding was observed and the original shape was lost.

[0076]

Table 3

	Crack Observation	Surface Strength	Ink Absorbability (s)	Water Resistance
Ex. 1	Good	Good	20	Good
Ex. 2	Good	Good	25	Good
Ex. 3	Good	Good	30	Good
Ex. 4	Good	Good	15	Good
Ex. 5	Good	Good	15	Good
Ex. 6	Good	Good	35	Good
Comp. Ex. 1	Poor	Poor	40	Good
Comp. Ex. 2	Unacceptable	Unacceptable	45	Unacceptable
Comp. Ex. 3	Unacceptable	Unacceptable	45	Unacceptable
Comp. Ex. 4	Inkjet recording material cannot be produced due to gelation of the coating liquid.			
Ex.: Example Comp. Ex.: Comparative Example				

[0077] As Table 3 clearly shows, as for the inkjet recording materials of Examples 1 to 6 prepared by the production method of the present invention, no cracks were observed on the surfaces of the ink receiving layers, and therefore, their high surface strength was confirmed. In addition, the inkjet recording material of the present invention had a high ink absorbability and a high water resistance, and therefore could produce fine images even in high-speed printing. Thus, the inkjet recording material prepared by the production method of the present invention exerts excellent effects: high porosity of the ink receiving layer enhances the ink absorbability; and the binder resin, even in a small amount, exhibits a strong binding force and therefore cracking on the surface of the ink receiving layer does not occur.

[0078] In Comparative Example 1, the inkjet recording material was prepared by the production method of the present invention, but the time from the addition of the crosslinking agent to the addition of the water-soluble basic compound was rather short and as a result the crosslinking reaction had not proceeded enough when the coating liquid was used. Therefore, the binder resin permeated the pores in the fine particles, and the loss in the amount of the binder decreased the surface strength and the ink absorbability.

[0079] Comparative Examples 2 and 3 lacked a saponified vinyl acetate-diacetone acrylamide copolymer and a crosslinking agent, respectively. The absence of crosslinking reaction caused problems in all of the evaluations regarding the surface strength, the ink absorbability, and the water resistance.

[0080] Comparative Example 4 lacked a water-soluble basic compound. As a result, during the processes of the preparation and coating of the ink receiving layer coating liquid, the crosslinking reaction proceeded too rapidly, which made it impossible to produce an inkjet recording material.

INDUSTRIAL APPLICABILITY

[0081] The method for producing an inkjet recording material of the present invention is highly productive because the viscosity of the coating liquid for preparing an ink receiving layer has an excellent stability, and cracking on the surface of the ink receiving layer does not occur during drying process. In addition, the inkjet recording material produced by the method of the present invention is excellent in ink absorbability, surface strength, and water resistance, and therefore can produce fine images even in high-speed printing.

Claims

1. A method for producing an inkjet recording material, the method comprising the steps of mixing an aqueous solution of a saponified vinyl acetate-diacetone acrylamide copolymer with a crosslinking agent to give a liquid mixture (a); adding a water-soluble basic compound to the liquid mixture (a) after a lapse of at least 30 minutes to give another liquid mixture (b); and mixing the obtained liquid mixture (b) with porous inorganic fine particles to give an ink receiving layer coating liquid and applying the coating liquid to a support, the inkjet recording material being **characterized in that** the ink receiving layer comprises the porous inorganic fine particles, the saponified vinyl acetate-diacetone acrylamide copolymer, and the crosslinking agent.

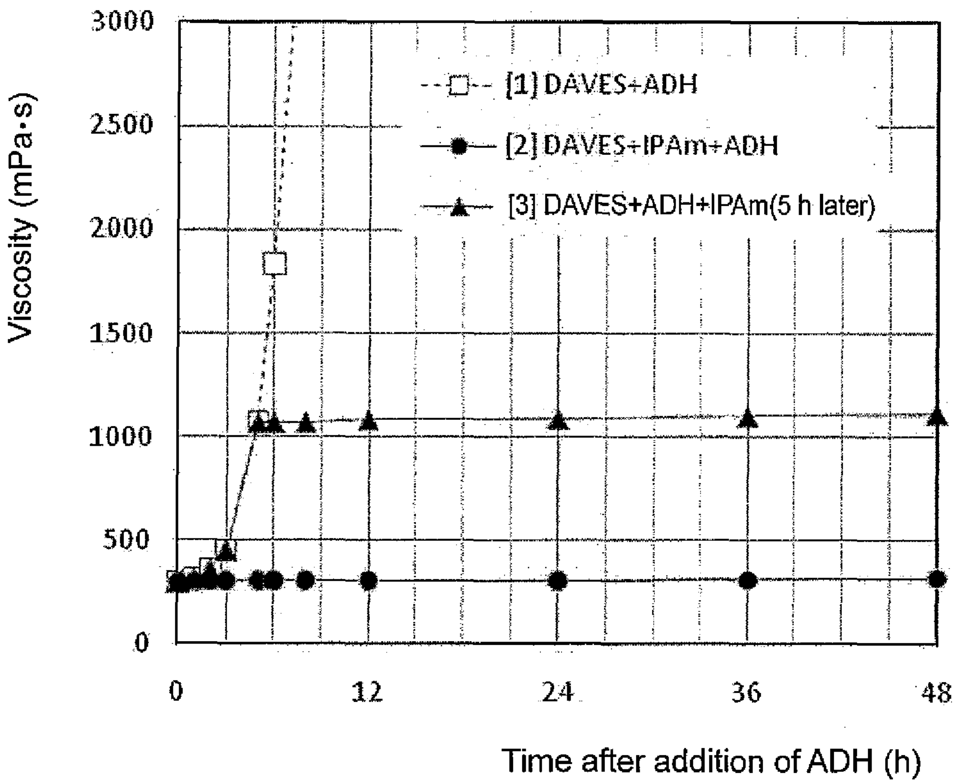
2. A method for producing an inkjet recording material, the method comprising the steps of mixing an aqueous solution of a saponified vinyl acetate-diacetone acrylamide copolymer with a crosslinking agent to give a liquid mixture (a); after the liquid mixture (a) has thickened, adding a water-soluble basic compound to the liquid mixture (a) and mixing them to give another liquid mixture (b); and mixing the obtained liquid mixture (b) with porous inorganic fine particles to give an ink receiving layer coating liquid and applying the coating liquid to a support, the inkjet recording material being **characterized in that** the ink receiving layer comprises the porous inorganic fine particles, the saponified vinyl acetate-diacetone acrylamide copolymer, and the crosslinking agent, and that the ratio of (B) the viscosity of the liquid mixture (b) immediately after the mixing with the water-soluble basic compound to (A) the viscosity of the liquid mixture (a) immediately after the mixing with the crosslinking agent [(B)/(A)] is 1.5 to 10.0.

3. The method of claim 1 or 2, wherein the crosslinking agent is a compound having 2 or more functional groups selected from the group consisting of hydrazino, hydrazide, and semicarbazide.

4. The method of any one of claims 1 to 3, wherein the water-soluble basic compound is one or more selected from the group consisting of ammonia and a water-soluble organic amine.

5. The method of any one of claims 1 to 4, wherein the viscosity of a 4% by weight aqueous solution of the saponified vinyl acetate-diacetone acrylamide copolymer measured by the method of JIS K-6726 (1994) is 10 to 100 mPa·s.

Fig. 1


3000
2500
2000
1500
1000
500
0
Viscosity (mPa·s)
[1] DAVES+ADH
[2] DAVES+IPAm+ADH
[3] DAVES+ADH+IPAm(5 h later)
0
12
24
36
48
Time after addition of ADH (h)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/074038

A. CLASSIFICATION OF SUBJECT MATTER

B41M5/00(2006.01)i, *B05D5/04*(2006.01)i, *B41M5/50*(2006.01)i, *B41M5/52*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B41M5/00, B05D5/04, B41M5/50, B41M5/52

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-335043 A (Fuji Photo Film Co., Ltd.), 25 November 2003 (25.11.2003), entire text (Family: none)	1-5
A	JP 2007-118533 A (Mitsubishi Paper Mills Ltd.), 17 May 2007 (17.05.2007), entire text (Family: none)	1-5
A	JP 2006-281474 A (Mitsubishi Paper Mills Ltd.), 19 October 2006 (19.10.2006), entire text (Family: none)	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 06 December, 2011 (06.12.11)	Date of mailing of the international search report 13 December, 2011 (13.12.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

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