

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 016 543 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

05.07.2000 Bulletin 2000/27

(51) Int. Cl.⁷: **B41M 5/00**

(21) Application number: **99126018.3**

(22) Date of filing: **27.12.1999**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **28.12.1998 JP 37314098**

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(54) **Recording medium, production thereof, and image formation employing the same**

(57) A recording medium comprising at least a base member, an ink-receiving layer containing alumina hydrate of a boehmite structure formed on the base member, and a porous layer containing particles and an alcohol-soluble organic polymer resin formed further on the ink-receiving layer.

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Description**BACKGROUND OF THE INVENTION**

5 Field of the Invention

[0001] The present invention relates to a recording medium suitable for recording with a liquid ink, particularly to a recording medium suitable for ink-jet recording. The present invention relates also to a process for producing the recording medium, and a process of image formation employing the recording medium.

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Related Background Art

[0002] The ink-jet recording system conducts recording by ejecting fine ink droplets and depositing the ink droplets onto a recording medium like a paper sheet to record a picture or letters. The ink-jet recording system has advantages of high speed printing with less noise generation, ease of multicolor printing, versatility in recording patterns, needlessness of development and fixation of images, and so forth. Therefore, the ink-jet recording system has come to be widely employed for image-recording in many applications such as information apparatuses. Further, a multicolor ink-jet system is capable of recording an image comparable with multicolor printing using plates, or color photography, and is capable of recording images at a lower cost than that of conventional multicolor printing and color photograph when the number of copies is small. The multicolor ink-jet system is coming to be employed widely in full-color image recording.

[0003] For the recording apparatus and the recording method of ink-jet recording system, various improvements have been made for speed-up of recording, fineness of the recorded images, full-color printing, and so forth. Additionally, the recording medium is also required to be improved. Hitherto, various types of recording mediums have been disclosed. For example, Japanese Patent Application Laid-Open No. 56-5830 discloses an ink-jet recording paper sheet which has an ink-absorbent coating layer on a base sheet; Japanese Patent Application Laid-Open No. 55-51583 employs amorphous silica as a pigment in a coating layer.

[0004] U.S. Patents 4,879,166 and 5,104,730, and Japanese Patent Application Laid-Open Nos. 2-276670, 3-215082, and 3-281383 disclose recording sheets having a porous ink-receiving layer containing alumina hydrate of a pseudo-boehmite structure. These disclosed ink-jet recording sheets are excellent in the quality and gloss of the recorded image. However, such an ink-receiving layer comprising alumina hydrate has disadvantages that its surface can be scratched readily, and that the recorded matter can be damaged by simple rubbing with cloth or paper.

[0005] For offsetting the disadvantage, Japanese Patent Application Laid-Open Nos. 3-67685, 6-183131, 7-76162, 7-101142, 7-117335, 8-2087, 8-2091, 8-2093, 8-183242, 9-66663, 10-129122, 10-166715, and so forth disclose a surface layer comprising silica, silica-alumina, or a fine particulate organic matter provided on an ink-receiving layer. However, the above methods have disadvantages as follows:

(1) The recording medium is produced by using a particulate inorganic or organic pigment, and a water-soluble polymer resin as a binder. However, in the above methods, the surface layer formed on the ink-receiving layer tends to have the particles packed densely, whereby the voids in the surface layer become smaller to retard the penetration of the ink and impair the image quality. For improvement thereof, Japanese Patent Application Laid-Open No. 6-183131 forms the voids with a surface layer not containing an organic polymer as a binder. In this method, however, the inorganic particles fall off readily from the surface layer to cause defects undesirably. Japanese Patent Application Laid-Open No. 3-67685 provides a porous ink-receiving layer on a transparent base member, and a coating pigment layer having an average particle size ranging from 1 to 15 μm is further provided thereon. In this method, however, the excessively large size of particles raises the opacity of the surface layer, whereby the printed image can be observed only from the base member side. Japanese Patent Application Laid-Open No. 10-166715 uses nonspherical silica particles to form voids in the silica layer. In this method, sharp protrusions of silica particles are formed to impair slidableness of the surface, tending to cause scratching and delivery failure.

(2) The water-soluble polymer resin contained in the surface layer can absorb moisture from the air to swell and become sticky when stored at a high temperature under high humidity, causing blocking or delivery failure of piled recording medium sheets. Japanese Patent Application Laid-Open Nos. 7-242055, 7-242057, and so forth provide a surface layer containing a water-insoluble alcohol-soluble polymer and particulate silica to prevent the blocking. However, for achieving sufficient anti-blocking properties and sufficient ink-absorbency, the particle size of the particulate silica should be larger, and should be contained in a larger amount in the surface layer, which can impair the transparency of the layer, and lower significantly the printed image density, and can cause powder-falling and cracks, undesirably. Further, since the ink-receiving layer is constituted mainly of a water-soluble polymer resin, the ink absorption rate is low, and bleeding and beading are liable to occur at a high-speed printing disadvantageously. Japanese Patent Application Laid-Open No. 8-290652 employs a highly alcohol-soluble organic compound is

applied on the surface of the alumina hydrate for forming the ink-receiving layer. This method is effective in preventing running of the ink, but is not effective in preventing the blocking or improving the deliverability. Moreover, in this method, the organic compound penetrates into the pores in the alumina hydrate layer to decrease the pore volume to impair remarkably the ink absorbency and to cause beading.

(3) In coating of the ink-receiving layer comprising alumina hydrate with an aqueous dispersion containing fine particles and a water-soluble polymer resin, bubbles are released from the voids in the ink-receiving layer, which roughens the dried surface layer to increase the opacity or causes cracking, impairing the quality of the recording medium.

SUMMARY OF THE INVENTION

[0006] The present invention has been accomplished to solve the above problems.

[0007] The present invention intends to provide a recording medium which gives a high image density, high ink absorption rate, high gradation of printing, high resistance against scratching, high deliverability without causing beading and printing irregularity, good transparency, and no blocking at a high temperature under high humidity.

[0008] The present invention intends also to provide an image formation process employing the above recording medium.

[0009] The present invention intends further to provide a process for producing the recording medium in which the coating liquid has high stability of the dispersion, and high productivity in the coating process.

[0010] The recording medium of the present invention comprises at least a base member, an ink-receiving layer containing alumina hydrate of a boehmite structure formed on the base member, and a porous layer containing particles and an alcohol-soluble organic polymer resin formed further thereon.

[0011] The image formation process of the present invention comprises ejecting ink droplets through a fine nozzle onto the above recording medium.

[0012] The process for producing a recording medium of the present invention having a porous ink-receiving layer formed on a base member, and a porous layer formed thereon comprises applying a liquid dispersion containing an alumina hydrate of a boehmite structure and a binder on a base member to form at least one porous ink-receiving layer followed by drying, and further applying another liquid dispersion containing an alcohol-soluble organic polymer resin and a particulate material dissolved in a solvent containing at least alcohol followed by drying to form a porous layer.

[0013] A recording medium of the invention gives a high image density, high ink absorption rate, high gradation of printing, high resistance against scratching, high deliverability without causing bending and printing irregularity, good transparency, and no blocking at a high temperature under high humidity. Furthermore, the coating has high stability of the dispersion, and high productivity in the coating process.

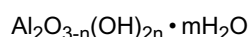
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] The ink-receiving layer of the recording medium of the present invention is formed as a porous layer comprising an alumina hydrate of a boehmite structure and a binder. The porous ink-receiving layer should have functions of receiving ink droplets ejected and deposited thereon by ink-jet recording, absorbing the solvent of the ink, and fixing the coloring matter such as a dye; should have high absorbency for preventing ink running and ink bleeding; and should have uniform layer quality for obtaining an image of photographic tone. In the present invention, the most suitable ink-receiving layer for formation of the porous layer thereon has a special fine porous structure containing a boehmite-structured alumina and a binder. This structure is suitable for high ink absorbency of the ink-receiving layer after forming the porous layer.

[0015] The alumina hydrate for the recording medium of the present invention is preferred as the material for the ink-receiving layer because the alumina hydrate is electrically positively charged to give high dye fixability to form images with high color developability and does not cause browning of a black ink, or lack of light-fastness.

[0016] The alumina hydrate contained in the ink-receiving layer of the recording medium of the present invention has preferably a boehmite structure as measured by X-ray diffraction in consideration of dye adsorption, ink absorption, and transparency.

[0017] The alumina hydrate is generally defined by the general formula below:



where n is an integer from 0 to 3, and m is a number from 0 to 10, preferably from 0 to 5; mH₂O represents usually water component not participating in formation of the crystal lattice and being releasable; m may not be an integer; and m and n are not simultaneously zero.

[0018] The process for production of the alumina hydrate of the boehmite structure to be contained in the ink-

receiving layer of the present invention is not specially limited. Any process which is capable of producing the alumina hydrate may be employed, including Beyer process, and an alum pyrolysis process. In a preferred process, an aluminum alkoxide of a long chain is hydrolyzed by addition of an acid: an alkoxide having 5 or more carbon atoms. In particular, the alkoxides having 12-22 carbon atoms are preferred further, since the alcohol component can be removed readily and the shape of the boehmite-structured alumina hydrate can be controlled readily. Compared with the production process for alumina hydrogels or cationic alumina, the above processes are advantageous in that impurities like ions are less liable to cause contamination. Furthermore, the aluminum alkoxide of long chains is advantageous in comparison with an alkoxide of short chains like aluminum isopropoxide, since the alcohol can readily be removed completely from the alumina hydrate after the hydrolysis.

[0019] The alumina hydrate prepared by the above process may be subjected to hydrothermal synthesis for particle growth, or may be dried into a powdery alumina hydrate.

[0020] Generally, the alumina hydrate crystal having a boehmite structure is a layered compound having the (020) plane as a giant plane, exhibiting a characteristic diffraction peak in the X-ray diffraction pattern. The boehmite structure includes the perfect boehmite structure and so-called pseudo-boehmite structures, the latter containing excess water between the layers of the (020) plane. The pseudo-boehmite exhibits a diffraction peak broader than that of the perfect boehmite. The perfect boehmite and the pseudo-boehmite cannot definitely be differentiated, so that the boehmite-structured alumina hydrate in the present invention includes the both type of boehmite, unless otherwise mentioned.

[0021] In the recording medium containing the alumina hydrate of the boehmite structure of the present invention, the alumina hydrate has its crystallinity ranging preferably from 15 to 80. Within this crystallinity range, the optical density of the printed portion is high, and ink running, ink beading, and ink crawling are less liable to occur.

[0022] The crystallinity mentioned above is the ratio of the X-ray diffraction intensity at $2\theta=10^\circ$ to that of a (020) plane around $2\theta=14-15^\circ$ of the pulverized recording medium in X-ray diffraction pattern by the $\text{CuK}\alpha$ line as described in Japanese Patent Application Laid-Open No. 8-132731 by the inventors of the present invention. The crystallinity thus obtained is a physical quantity corresponding to the ratio of the crystalline portion to the noncrystalline portion of the alumina hydrate in the recording medium. "Running of ink" in the present invention signifies the spreading (expansion) of the area of a dyed portion of a prescribed solid print area. "Beading" signifies irregularity in a granular shape in density caused by coalescence of the ink droplets in the solid print area. "Crawling" signifies occurrence of non-colored portion in the solid print area. The degree of parallelization between the microcrystal of the boehmite-structured alumina hydrate and the plane direction of the ink-receiving layer is preferably not less than 1.5. The degree of parallelization is defined in Example described later under the heading of "crystallinity". The circularity of the printed dots is good at the parallelization degree of not less than 1.5, whereas it is poor at the parallelization degree of less than 1.5.

[0023] The shape of the boehmite-structured alumina hydrate particles can be observed by transmission electron microscopy with a test sample prepared by dropping a dispersion of the alumina hydrate in water, alcohol, or the like onto a collodion film. Of the alumina hydrates, pseudo-boehmite is known to include a cilium-shaped type, and the other types as shown in a report (Rocek J., et al: Applied Catalysis, vol.74, pp.29-36, 1991). In the present invention, either the cilium-shaped type or plate type can be used. The shape of the alumina hydrate particles (particle shape, particle diameter, and aspect ratio) can be measured by transmission electron microscopy with a test sample prepared by dropping a dispersion of the alumina hydrate in deionized water onto a collodion film.

[0024] From the knowledge of the inventors of the present invention, the alumina hydrate in a flat plate shape is preferred to the one in a hair bundle shape (cilium shape), since the alumina hydrate in a flat plate shape has higher dispersibility in water, gives a larger pore volume by random orientation of the alumina hydrate particles in the formed ink-receiving layer, and gives a broader distribution of the pore size. "Hair bundle shape" herein signifies a state of assemblage of needle-shaped alumina hydrate particles in a shape of hair bundle with their side faces contacting together.

[0025] The aspect ratio is a ratio of the diameter to the thickness of a particle. The aspect ratio of the plate-shaped particle can be measured by the method defined in Japanese Patent Publication No. 5-16015. The diameter herein is a diameter of a circle having an area equal to the projected area of a particle in observation of the alumina hydrate by an optical or electron microscope. The length/breadth ratio is a ratio of the largest diameter to the smallest diameter when observed in the same manner as the aspect ratio. The aspect ratio of the hair bundle shape can be obtained by measuring the diameters and the lengths at the ends of a needle-shaped particle of individual alumina hydrate as a column, and taking the ratio of the length to the diameter.

[0026] The alumina hydrate in a flat plate shape has preferably an average aspect ratio ranging from 3 to 10 and an average particle diameter ranging from 1 to 50 nm; the aluminum hydrate in a hair bundle shape has preferably an aspect ratio ranging from 3 to 10 and an average particle diameter ranging from 1 to 50 nm. Within the above average aspect ratio, interstices are formed between particles in formation of an ink-receiving layer or on addition into a fibrous material, thereby a porous structure being readily formed with broad distribution of the pore radius. Within the above range of the average particle diameter or the average particle length, porous structure can be formed with a large pore volume. At the average aspect ratio lower than the lower limit of the above range, the pore diameter distribution in the ink-receiving layer will be narrow, whereas at the average aspect ratio higher than the upper limit of the above range,

alumina hydrate cannot be prepared with uniform particle diameter. At the average particle diameter or the average particle length smaller than the lower limit of the above range, the pore diameter distribution tends to be narrow, whereas at the value larger than the above upper limit, the absorbency for the printed dye tends to be low.

[0027] The pore properties of the alumina hydrate can be adjusted in the production process. To produce the recording medium satisfying the conditions of the BET specific surface area and the pore volume of the ink-receiving layer as mentioned later, the alumina hydrate preferably has a pore volume ranging from 0.1 to 1.0 cm³/g. The alumina hydrate having a larger pore above the range volume tends to cause cracking or powder-falling, whereas the alumina hydrate having a smaller pore volume below the range tends to cause a decrease in ink absorbency, ink running, and feathering of the image, in particular, in multicolor printing.

[0028] The BET specific surface area of the alumina hydrate ranges preferably from 40 to 500 m²/g. A smaller BET specific surface area, below the range, of the alumina hydrate tends to increase haze in the ink-receiving layer to cause white fogging of the image. A larger BET specific surface area above the range tends to cause cracking in the ink-receiving layer.

[0029] The pore volume of the ink-receiving layer ranges preferably from 0.1 to 1.0 cm³/g. A larger pore volume, above the range, of the ink-receiving layer is liable to cause cracking or powder-falling of the layer and to decrease its transparency to lower the image density. A smaller pore volume, below the range, of the ink-receiving layer tends to decrease the ink absorbency of the layer to cause ink running, and feathering of the image, in particular, in multicolor printing.

[0030] The BET specific surface area ranges preferably from 20 to 450 m²/g. A smaller BET specific surface area below the range tends to increase haze in the ink-receiving layer to cause fogging of the image. A larger BET specific surface area above the range tends to cause cracking in the ink-receiving layer.

[0031] The BET specific surface area and the pore volume mentioned above is measured by adsorption and desorption of nitrogen with a sample having been deaerated at 120°C for 24 hours.

[0032] The pore structure of the ink-receiving layer can be measured by a nitrogen absorption method or a mercury pressure-penetration method. The pore radius distribution has a maximum peak preferably in the range from 2.0 to 20.0 nm. Within this range, both the ink absorption rate and the dye fixation rate can be raised without occurrence of running or bleeding of the ink. With the maximum peak radius exceeding the above range, the dye fixation rate may be decreased to cause ink running or to lower the circularity of the printed dots. With the maximum peak radius less than the above range, the ink absorption rate may be low.

[0033] The pore structure is selected to be suitable for the purpose. Japanese Patent Publication No. 7-2430 discloses a recording medium having an ink-receiving layer comprising pseudo-boehmite in which the total volume of the pores within the range from 10 to 100 nm is not more than 0.1 cc/g. Japanese Patent No. 2714352 discloses a recording medium having an ink-receiving layer having an average pore radius ranging from 2.0 to 20.0 nm and the half breadth of the pore radius distribution ranging from 2.0 to 15.0 nm. Japanese Patent No. 2714350 discloses a recording medium having pore radius distribution peaks at a radius of not more than 10.0 nm and in the radius range from 10.0 to 20.0 nm. Japanese Patent Application Laid-Open No. 5-323037 discloses a recording medium having a ink-receiving layer of two-layered pseudo-boehmite structure constituted of a lower layer having an average pore diameter ranging from 2 to 8 nm and a thickness ranging from 5 to 60 μm and an upper layer having an average pore diameter ranging from 4 to 15 nm and a thickness ranging from 2 to 30 nm. Japanese Patent Application Laid-Open No. 9-66664 discloses a recording medium having an ink-receiving layer which has cavities inside communicating through a small pores with the surface of the ink-receiving layer. The above disclosed pore structure of the porous layer, when employed in the present invention as the ink-receiving layer, will respectively be effective in broadening of the ink selection range, increase of the transparency, increase of the ink absorbency, prevention of ink running, prevention of blurring of the prints, improvement of absorbency in multicolor printing, and so forth. Furthermore, the porous layer formed thereon enables further improvement of the above effects.

[0034] The pore structure of the ink-receiving layer does not depend on the properties of the alumina hydrate employed, but depends on the production conditions such as the type and the amount of the binder; the concentration, viscosity and dispersion state of the coating liquid; the coating apparatus; the coating head; the coating amount; the flow rate, temperature, and flow direction of the drying air flow; and so forth. Therefore, the production conditions should be controlled to be in the optimum range to obtain the desired properties of the ink-receiving layer in the present invention.

[0035] The recording medium in the present invention may contain an additive as necessary. The additive may be selected arbitrarily from metal oxides, salts of divalent or higher valent metal, and cationic organic compounds. The metal oxides preferably include titanium dioxide and silica as described in Japanese Patent No. 2714351, boria, silica-boria, magnesia, silica-magnesia, zirconia, and zinc oxide, and hydroxides. The divalent or higher valent metal salts preferably includes salts such as calcium carbonate, and barium sulfate; halide salts such as magnesium chloride, potassium bromide, calcium iodide, zinc chloride, zinc bromide, and zinc iodide; calcium nitrate; kaolin; and talc. The cationic organic compounds preferably include quaternary ammonium salts, polyamines, and alkylamines. The amount

of the additive to be contained is preferably not more than 20% by weight of the alumina hydrate.

[0036] Two or more kinds of binder may be used in the present invention. The binder may be selected arbitrarily from water-soluble polymers and water-dispersible polymers. The polymers preferably include water-soluble polymers such as modified or unmodified polyvinyl alcohols, modified or unmodified starch, modified or unmodified gelatin, modified or unmodified casein, gum arabic, cellulose derivatives like carboxymethylcellulose, polyvinylpyrrolidone, maleic anhydride or copolymers thereof, and acrylate ester copolymers; and water-dispersible polymers such as conjugate diene type copolymer latexes like SBR latexes, and vinyl type copolymer latexes like functional-group-modified polymer latexes and an ethylene-vinyl acetate latex. Of these polymers, polyvinyl alcohols are widely used in view of the water absorbency and the transparency. The resin emulsion can be used suitably in view of the dispersion of the alumina hydrate and the water absorbency and water resistance of the recording medium as mentioned in Japanese Patent Application Laid-Open Nos. 8-325992 and 10-94754.

[0037] The mixing ratio of the alumina hydrate to the binder ranges preferably from 1:1 to 30:1 by weight. Within this range, the ink absorption rate of the medium is high, and the optical density of the printed portion is high. With the amount of the binder less than that, the mechanical strength of the ink-receiving layer is not sufficient, tending to cause cracking or powder-fall. With the amount of the binder more than that, the pore volume may be small to cause drop of the ink absorbency. In consideration of the ink absorbency and the less tendency of cracking on bending, the above amount of the binder is more preferably in the range from 3:1 to 20:1.

[0038] In the present invention, the ink-receiving layer may contain, in addition to the alumina hydrate and the binder, an additive such as a pigment dispersant, a thickening agent, a pH-controlling agent, a lubricant, a fluidity modifier, a surfactant, an anti-foaming agent, a waterproofing agent, a foam-inhibitor, a releasing agent, a foaming agent, a penetrating agent, a coloring dye, a fluorescent whitener, a UV absorber, an antioxidant, an antiseptic agent, and a mildew-proofing agent. For example, suitably used are melamine type materials and aldehyde type materials for raising the surface tension of the liquid dispersion or for promoting the film formation; crosslinking agents such as boric acid, and borates for crosslinking the binder; solvents having a boiling point in the range from 100°C to 180°C higher than that of the dispersion medium, such as methylcellosolve, ethylcellosolve, propylene glycol monomethyl ether, DMF, and ethylene glycol and propylene glycol and esters thereof. As the water-proofing agent, quaternary ammonium halides, quaternary ammonium salt polymers can be used without limitation.

[0039] The base member for formation of the ink-receiving layer in the present invention includes paper sheets such as suitably sized paper sheets, non-sized paper sheets, and resin-coated paper sheets coated with polyethylene of the like; and thermoplastic resin films, without limitation. The thermoplastic resin film includes transparent sheets of polyester, polystyrene, polyvinyl chloride, polymethyl methacrylate, cellulose acetate, polyethylene, and polycarbonate; and opaque sheet made opaque by filling of a filler or by fine foaming.

[0040] The recording medium of the present invention can be produced by any conventional process for alumina hydrate coating, without special limitation. The alumina hydrate is dispersed in water and is applied onto a base member. If necessary, a heat treatment may be additionally conducted as described in Japanese Patent Application Laid-Open No. 9-86035.

[0041] The dispersion treatment of the liquid dispersion containing the boehmite-structured alumina hydrate and the binder can be conducted by any of conventional dispersion processes. Specifically, a suitably used machine includes a grinding type of dispersion machines such as a ball mill and a sand mill, and an agitation type of dispersion machines such as a homomixer and a homodisperser.

[0042] The porous layer of the recording medium of the present invention is provided for modifying the surface properties of the ink-receiving layer not only to improve the deliverability and the anti-blocking properties, but to allow the ink components of the deposited recording ink to permeate quickly into the porous layer to be absorbed by the ink-receiving layer without impairing the recording properties of the ink-receiving layer, to improve the image density, the color tone, and the resolution, and to prevent beading. For this purpose, the porous layer should have high transparency and high ink permeability.

[0043] The particle employed in the present invention is preferably dispersible and suspendible in a colloidal state in the liquid medium, and is capable of forming, in the coating film, pores for securing the ink permeability with less light-scattering.

[0044] The diameter of the particles ranges preferably from 10 nm to 100 nm. The particles having a diameter smaller than the above range may plug the pores on the surface to decrease the pore volume and the pore radius of the entire recording medium to retard the ink permeation and to cause ink running, ink bleeding, beading, and so forth. The particles having a diameter larger than the above range may decrease the transparency of the surface layer to cause white fogging of the printed image, or may reduce the image definition to decrease the sharpness of the image.

[0045] For the porous layer of the present invention, the shape of the particles is preferably spherical. The spherical particles serve to improve surface slip properties and to retard tacking, thereby making the recording medium resistant to scratching on rubbing, decreasing the static friction between the piled sheets in cassette type feeding of the paper sheets without delivery failure or double-sheet feeding. On the other hand, the nonspherical particles are liable to form

sharp protrusions on the outermost surface of the sheet to increase the static friction of the surface, making less resistant to scratching, or causing sheet delivery failure.

[0046] The particles employed in the present invention are preferably dispersible stably in alcohol. The particles stable only in water will convert the entire liquid dispersion into a large gel when an alcohol-soluble organic polymer resin of the present invention is added thereto as a binder, thereby making impracticable the formation of the coating film. It was found by the inventors of the present invention that, when an aqueous dispersion containing the particles and a water-soluble polymer resin is applied onto an ink-receiving layer having a larger pore diameter or a larger pore volume for the higher ink absorbency, the air existing in the voids of the ink-receiving layer will penetrate in a state of fine bubbles into the coating liquid, and the bubbles burst during the drying process to form cracks in the layer or to roughen the surface, or the remaining air in the layer will make the layer opaque, thereby lowering the printed image density or impairing the printed image quality. On the other hand, when a liquid dispersion containing the particles dispersed in alcohol and an alcohol soluble organic polymer resin is applied for coating, no bubble is formed even on an ink-receiving layer having a larger pore diameter or a pore volume, whereby a transparent coating film can be formed without cracking. Presumably, the alcohol employed weakens the surface tension of the liquid dispersion to facilitate penetration of the alcohol into the voids in the ink-receiving layer to accelerate replacement of the air and retarding the bubble formation.

[0047] Any alcohol-dispersible particulate matter is applicable which is dispersible in an alcohol or an alcoholic solvent mixture containing a minor amount of water or other organic solvent. Specifically, the particulate material includes inorganic pigments such as colloidal silica, colloidal alumina, titania sol, zirconia sol, and zinc oxide sol; organic particulate pigments which do not melt together during the coating film formation, including pigments containing a polymer such as polystyrene, polymethyl methacrylate, styrene-butadiene copolymers, methyl methacrylate-butadiene copolymers, acrylate ester-methacrylate ester copolymers, styrene-acrylate ester copolymers, microcapsules, and beads of resins, e.g., urea resins, and melamine resins.

[0048] Among the above alcohol-dispersible particulate matters, preferred is colloidal silica, more specifically organosilica sol, and water-dispersible silica sol which is not destroyed by addition of an alcohol: for example, acidic silica sol, composite silica sol modified on the surface with an aluminum oxide, particulate silica modified at the surface by introduction of organic group by use of a coupling agent, a chelating agent, or a metal alkoxide, and so forth, since they combine well with the alcohol-soluble organic polymer resin to form a hard surface film and to retard the particle-falling or powder-falling owing to insufficient bonding properties of the binder.

[0049] The binder preferably used for the porous layer in the present invention includes alcohol-soluble organic polymer resins, since the alcohol-soluble organic polymer resin is effective in improving the water-resistance and preventing the beading. When a water-soluble polymer resin is used as the binder, the water-resistance of the layer is lowered by the solubleness of the coating layer, the printed dots are spread owing to the water contained as the major portion of the ink to promote ink-running, and beading is liable to be caused in solid print. However, the alcohol-soluble organic polymer resin is water-resistant, and is capable of giving sharp dots without running of the ink without beading. The ink contains alcohols such as isopropyl alcohol, glycerin, and ethylene glycol for prevention of nozzle clogging and for stable ink ejection. The alcohols, which is contained in the ink at a content much lower than that of the water, cannot dissolve the surface layer. The use of the alcohol-soluble organic polymer resin is effective in increasing the affinity with the ink to improve the ink permeability, and in improving the anti-blocking property under high temperature and high humidity. When a water-soluble polymer is used, the surface portion can be swollen by the moisture in the air to result in tackiness of the surface, whereby the sheets may be blocked to prevent the separation of the sheets when stored under high temperature and high humidity like in the summer or the rainy season. The blocking of the sheets can be prevented by providing on the outermost portion a matting agent having a large particle size. However, this method is not advantageous since the transparency of the ink-receiving layer is impaired, and the image density and the image definition are lowered by this method. On the other hand, the use of the alcohol-soluble organic polymer resin scarcely causes swelling of the layer by air moisture, not causing sheet blocking.

[0050] The liquid dispersion of particles dispersed in alcohol and an alcohol-soluble organic polymer resin can be dried quickly on coating on the ink-receiving layer to form a porous layer, thereby coating speed being raised to improve the productivity remarkably. Moreover, the particles are less liable to agglomerate together, and the dispersion forms the coating layer containing the particles dispersed uniformly without cracking. Furthermore, the extremely quick drying in the coating process evaporates a large amount of the solvent to form many communication holes in the interstices between particles from the ink-receiving layer to the surface of the porous layer to promote the ink permeability, giving a recording medium excellent in ink absorption rate and anti-beading property.

[0051] To the contrary, when a liquid dispersion containing particles dispersed in water and a water-soluble polymer resin is applied on the ink-receiving layer, the particles can agglomerate together in the liquid dispersion or during the film formation, which can cause cracking in the coating film, or can cause migration of the binder to the outermost surface to retard the formation of the communication holes in the porous layer on the surface. This binder migration can decrease substantially the pore radius and the pore volume in the entire layers including the ink-receiving layer to

decrease the ink permeability or the ink absorption capacity disadvantageously.

[0052] The alcohol-soluble organic polymer resin employed for the above purpose is not limited specially, provided that it is soluble in alcohol, specifically including alcohol-soluble nylon and copolymers thereof, polyvinylacetal, polyvinylbutyral, polyvinyl acetate and copolymers thereof, polyacrylic resins and copolymers thereof, methylcellulose, ethylcellulose, ethylene-vinyl copolymer, polyacrylic ester and copolymer thereof. One or more resins may be selected from the above resin group.

[0053] For dissolving the binder and dispersing the particles, the solvent may be a simple alcohol or a mixed solvent of an alcohol and water or another organic solvent. In the mixed solvent, the mixing ratio of the alcohol to the other solvent is decided suitably depending on the solubility of the binder and dispersibility of the particles, and is not limited specially. In order to prevent the aforementioned bubble generation during the application of the coating liquid onto the ink-receiving layer, the alcohol is preferably contained in the mixed solvent at a content of not less than 30% by weight based on the entire mixed solvent. The type of the alcohol is not limited specially, provided that the alcohol is capable of dissolving the binder resin: specifically including alkyl alcohols having 1-6 carbon atoms such as methyl alcohol; ketone alcohols such as diacetone alcohol; polyalkylene glycols such as polyethylene glycol; alkylene glycols of 2-6 carbon alkylene group such as ethylene glycol; glycerin; and lower alkyl ethers of a polyhydric alcohol such as ethylene glycol methyl ether. One or more of the above solvents may be suitably used arbitrarily.

[0054] The mixing ratio of the particles and the binder ranges preferably from 1:1 to 30:1 by weight. Within this range, the surface of the porous layer has satisfactory slip properties and less tackiness, and is less liable to cause beading. With the amount of the binder less than the above range, the mechanical strength of the porous layer is insufficient, and cracking and powder-falling are liable to occur. With the amount of the binder more than the above range, the voids in the porous layer may become smaller to result in lower ink permeability. In consideration of the high ink permeation rate and the high surface hardness, the above ratio is more preferably in the range from 3:1 to 20:1.

[0055] In the present invention, the porous layer may contain, in addition to the particles and the binder, an additive such as a pigment dispersant, a thickening agent, a pH-controlling agent, a lubricant, a fluidity modifier, a surfactant, an anti-foaming agent, a waterproofing agent, a foam-inhibitor, a releasing agent, a foaming agent, a penetrating agent, a coloring dye, a fluorescent whitener, a UV absorber, an antioxidant, an antiseptic agent, and a mildew-proofing agent.

[0056] The liquid dispersion containing the particles and the binder may be prepared in any of conventional dispersion method. Specific examples of the dispersion apparatuses include attrition type dispersion machines such as ball mills and sand mills, and agitation type dispersion machines such as homomixer and homodisperser.

[0057] The application of the coating liquid for formation of the porous layer and the ink-receiving layer may be conducted by use of a conventional apparatus such as a blade coater, an air knife coater, a roll coater, a brush coater, a curtain coater, a bar coater, a gravure coater, a die coater, and a sprayer.

[0058] For the ink-receiving layer formation, the amount of the application of the liquid dispersion is in the range preferably from 0.5 to 60 g/m² in terms of solid content in view of the ink absorption capacity, more preferably from 5 to 45 g/m² in view of higher ink absorption rate and prevention of cracking and powder-falling.

[0059] For the porous layer formation, the amount of the application of the liquid dispersion is in the range preferably from 0.05 to 20 g/m² in terms of solid content for keeping the transparency and imparting the slip properties and anti-blocking properties, and more preferably from 0.5 to 15 g/m² for improving the ink permeability and prevention of bronze-like gloss irregularity.

[0060] The porous layer of the present invention is made from particles and an alcohol-soluble organic polymer resin. Thereby, many communication holes are formed through the porous layer from the outermost surface to the ink-receiving layer with the high transparency retained to achieve high ink permeation rate. Further, the porous layer provided on the ink-receiving layer improves the recording medium in scratch resistance, anti-blocking properties, deliverability, and water-resistance.

[0061] The recording medium produced as above should be capable of absorbing the ink in a larger amount at a higher absorption rate to meet the requirements for the ink-jet printer for high-quality printing as the silver salt photograph. This type of ink-jet printer conducts image formation at a high dot density by overlapping dots of inks of different dye concentrations to obtain smooth gradation from highlight to shadow portions. Further, for high-speed printing, a larger amount of ink is applied in a high density in one scan by decreasing the number of the paths of the multi-path. For adapting to such a printer, the recording medium should be capable of absorbing the ink at a high speed in a large amount. In particular, after printing in one scanning with the head, the ink component should be completely absorbed before the subsequent scanning for printing. For realizing this, the ink applied at a resolution of 600dpi×600dpi and a density of 5.0×10^{-3} mL/inch² should be absorbed within one second. If the ink absorption time of the recording medium is longer than the time mentioned above, the ink remains unabsorbed on the recording medium during the printing to cause mixing of the ink on the surface, resulting in beading, and bleeding of the ink, and making the gradation less smooth, and further, streaking irregularity corresponding to the head scanning is liable to be caused. The recording medium of the present invention has communication holes formed as described above in the porous layer. These communication holes allow the ink to penetrate at a high speed and to fix in the ink-receiving layer, and serves to diffuse

and evaporate the solvent component. Therefore, the communication holes are not filled by the ink, thereby keeping the permeability and enabling high-speed ink absorption.

[0062] For the aforementioned high-speed ink absorption, the total pore volume in the entire of the porous layer and the ink-receiving layer ranges preferably from 0.1 to 1.0 cm³/g. The pore volume larger than the above range will decrease the transparency to cause white fogging of the image or decrease of resolution or sharpness of the image after recording. The pore volume smaller than the above range will lower the ink absorption rate remarkably and tends to allow the ink to run to cause feathering of the image, especially in multicolor printing.

[0063] The ratio (PV2/PV1) of the overall pore volume (PV2) of the ink-receiving layer and the porous layer to the pore volume (PV1) of the ink-receiving layer ranges preferably from 0.6 to 1.5. The pore volume ratio larger than the above range may decrease the transparency to result in a low image density after printing, or may cause ink running. The pore volume smaller than the above range may decrease the ink absorbency to cause crawling of the ink or deformation of the circular dot shape.

[0064] The maximum peak of the pore radius distribution of the entire layers including the porous layer and the ink-receiving layer ranges preferably from 2.0 to 20.0 nm. The peak radius larger than the above range may cause light scattering in the layers to increase the haze, resulting in white fogging of the image. The fine peak radius smaller than that may lower the ink absorption rate to cause beading, or bleeding in the image border.

[0065] The ink used in the image formation in the present invention composed mainly of a coloring agent (dye or pigment), a water-soluble organic solvent, and water. The dye is preferably a water-soluble dye such as direct dyes, acid dyes, basic dyes, reactive dyes, and food dyes, but is not specially limited thereto provided that the dye has required properties for fixability, color-developability, sharpness, stability, light-fastness, and other properties in combination with the above recording medium.

[0066] The water-soluble dye is used as a solution in a solvent composed generally of water or water and a water-soluble organic solvent. The solvent is preferably a mixture of water and a water-soluble organic solvent. The water content is preferably adjusted to be in the range from 2.0 to 90% by weight of the ink.

[0067] The useful water-soluble organic solvent includes alcohols having 1-4 carbon atoms such as methyl alcohol; amides such as dimethylformamide; ketones and ketone alcohols such as acetone; ethers such as tetrahydrofuran; polyalkylene glycols such as polyethylene glycol; alkylene glycols having an alkylene group of 2-6 carbon atoms such as ethylene glycol; glycerin; lower alkyl ethers of a polyhydric alcohol such as ethylene glycol methyl ether. Of the water-soluble organic solvents, preferred are polyhydric alcohols such as diethylene glycol; lower alkyl ethers of polyhydric alcohol such as triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether. Polyhydric alcohols are particularly preferred since they are effective as a lubricant for preventing clogging of nozzles owing to deposition of the water-soluble dye by evaporation of water in the ink.

[0068] A solubilizer may be added to the ink. Typical solubilizers are nitrogen-containing heterocyclic ketones. The solubilizer is used to improve remarkably the solubility of the water-soluble dye in the solvent. N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone are preferred as the solubilizer. Further, other additives may be added for improving the properties of the ink. The additives include surfactants for raising permeability of the ink component into a plain paper sheet, viscosity-controllers, surface tension controlling agents, and resistivity controlling agents.

[0069] Image formation is conducted on the above recording medium with the above ink by an ink-jet recording system. Any ink-jet system may be employed which discharge ink effectively through a nozzle to deposit the ink on a recording medium. The ink-jet system disclosed in Japanese Patent Application Laid-Open No. 54-59936 is useful in which the ink is ejected through a nozzle by a driving force generated by quick volume change of the ink by thermal energy.

[Examples]

[0070] The present invention is described more specifically by reference to Examples without limiting the present invention.

[0071] The physical properties of the material employed in the present invention were measured by the methods shown below.

[Properties of Ink-Receiving Layer]

[0072]

1. Crystallinity, and parallelization degree:

The recording medium in a sheet state, or the ink-receiving layer separated from the recording medium and pulverized were subjected to X-ray diffraction. From the X-ray diffraction pattern, were obtained the intensity at 2θ=10°, and the peak intensities of the (020) plane and the (120) plane. Further, from the X-ray diffraction pattern

of the ink-receiving layer separated from the recording medium, were obtained the peak intensities of the (020) plane and the (120) plane. The crystallinity and the parallelization degree were obtained according to the equations below:

$$\text{Crystallinity} = \text{Peak intensity of (020) plane} / \text{Intensity at } 2\theta = 10^\circ$$

$$\text{Intensity Ratio of Powder} = \text{Peak intensity of (020) plane of powder} / \text{Peak intensity of (120) plane of powder}$$

$$\begin{aligned} & \text{Intensity ratio of medium (ink-receiving layer)} \\ & = \text{Peak intensity of (020) plane of medium} / \text{Peak intensity of (120) plane of medium} \end{aligned}$$

$$\text{Parallelization degree} = \text{Intensity ratio of medium} / \text{Intensity ratio of powder}$$

The X-ray diffraction measurement was conducted under the conditions below:

Measurement apparatus: RAD-2R (Rigaku Denki K.K.)

Target: CuK α

Optical system: Wide-angle goniometer (with curved graphite monochromator)

Gonio radius: 185 mm

Slits: DS1° RS1° SS0.15mm

X-ray output: 40 kV, 30 mA

Measurement conditions: 2 θ - θ method

Continuous scanning at an interval of 2 θ =0.02° 2 θ = 10-90°, 2°/min

2. BET specific surface area, maximum peak of pore diameter, and pore volume:

The recording medium provided with alumina hydrate and an ink-receiving layer only was desecrated by sufficient heating, and was subjected to measurement by nitrogen adsorption-desorption method.

Measurement apparatus: Autosorb 1 (Quantachrome Co.)

2-1. The BET specific surface area was calculated by the method of Brunauer, et al. (J.Am.Chem.Soc., vol.60, p.309, 1938).

2-2. The pore radius, and the pore volume were calculated by the method of Barrett (J.Am.Chem.Soc., vol.73, F.373, 1951). The maximum peak of the pore radius was derived from the pore radius distribution.

3. Particle shape:

A dispersion of alumina hydrate in deionized water was dropped onto a collodion film to prepare a test sample. This sample was observed by transmission type electron microscope (H-500, Hitachi, Ltd.), and the aspect ratio and the particle diameter were measured.

4. Dispersion state of coating liquid:

The dispersion state was evaluated visually. A dispersion which was in a good colloid state without gelation and precipitation was evaluated as "A" (good). The dispersion which was in a poor dispersion state with gelation or precipitation formation was evaluated as "C" (poor).

5. Transparency:

An ink-receiving layer was formed on a transparent PET film. This sample was subjected to measurement of total light transmittance (%) with a haze meter (NDH-1001DP, Nippon Denshoku K.K.) according to JIS K-7105.

6. Crack:

An ink-receiving layer was formed on a transparent PET film. This sample was examined visually for presence of cracks. The sample which had no crack was evaluated as "A" (good). The sample which did not have a crack or cracks of not less than 5 mm was evaluated as "B" (fair). The sample which had a crack or cracks of not less than 5 mm was evaluated as "C" (poor).

[Physical Properties of Recording Medium]

[0073]

1. BET specific surface area, Maximum peak of pore radius, and Pore volume:

The recording medium was heated and deaerated sufficiently, and was subjected to measurement by a nitrogen adsorption-desorption method in the same manner as shown in the above item 2 of "Properties of Ink-Receiving Layer".

2. Dispersion state of coating liquid:

The dispersion state was evaluated visually. A dispersion which was in a good colloid state without gelation and precipitation was evaluated as "A" (good). The dispersion which was in a poor dispersion state with gelation or precipitate formation was evaluated as "C" (poor).

3. State immediately after coating:

The phenomena occurring immediately after application of the coating liquid for formation of the layer on the ink-receiving layer were observed visually. The state in which the coating liquid was uniformly applied without bubble formation was evaluated as "A" (good). The state in which bubbles were formed, or crawling occurred on coating liquid application was evaluated as "C" (poor).

4. Transparency:

A sample was prepared by forming an ink-receiving layer and a porous layer on a transparent PET film. This sample was subjected to measurement of total light transmittance (%) with a haze meter (NDH-1001DP, Nippon Denshoku K.K.) according to JIS K-7105.

5. Crack:

An ink-receiving layer and a porous layer were formed on a transparent PET film. This sample was examined visually for presence of cracks. The sample which had no crack was evaluated as "A" (good). The sample which did not have a crack or cracks of not less than 5 mm was evaluated as "B" (fair). The sample which had a crack or cracks of not less than 5 mm was evaluated as "C" (poor).

6. Powder-falling:

The powder-falling of the printed face of the recording medium was evaluated by means of a Gakushin type friction tester Model II (Tester Sangyo K.K.). A piece of a black flock paper sheet was set to the arm of the tester with a weight of 300 g placed thereon. A sample test piece was set on the vibration table with the printed face directed upward. The printed face was rubbed 20 times. The reflection densities of black color at the rubbed portion and the non-rubbed portion of the flock paper sheet were measured by a reflection-densitometer 310TR (X-Rite Co.). The black density remaining ratio was derived from the density difference according the equation below. The sample exhibiting the remaining ratio of 80% or higher was evaluated as "A" (good); lower than 80% but not lower than 40%, as "B" (fair); and lower than 40% , as "C" (poor)".

Remaining ratio (%)

$$= [1 - \{(Density\ at\ rubbed\ portion - Density\ at\ non-rubbed\ portion) / (Density\ at\ non-rubbed\ portion)\}] \times 100$$

7. Surface hardness:

The pencil hardness of the printed face of the recording medium was measured according to JIS K-5400.

8. Anti-blocking property:

Ten sheets of the recording medium were piled on a table, and thereon a glass plate of the same size weighing 1 kg was placed. The piled recording medium was stored under a condition of 30°C and 80%RH for one month. After the storage, the recording medium which could be separated without blocking was evaluated as "A" (good), and the recording medium which could not be separated by blocking was evaluated as "C" (poor).

9. Friction coefficient:

The friction coefficients of the front face and the back face of the recording medium were measured according to JIS P-8147.

10. Scratch resistance:

The test piece after the above friction coefficient measurement was examined visually for the presence of scratch. The sample which did not scratched was evaluated as "A" (good). The sample which was scratched was evaluated as "C" (poor).

11. Tackiness:

The surface of the recording medium was touched with a finger. The recording medium which was not tacky by finger touch was evaluated as "A" (not tacky). the recording medium which was tacky by finger touch was evaluated

as "C" (tacky).

12. Printing properties:

Ink-jet recording was conducted with a drop-on-demand type ink-jet printer provided with an ink-jet head having nozzles at an interval of 24 nozzles per 1 mm (600 dpi) for the respective colors by scanning in the direction perpendicular to the nozzle arrangement direction. The inks of the composition shown below were used. The ink was ejected in an amount of 10 pL for one dot printing. The amount of the ink in mono-color printing at 24×24 dots per 1 mm² (600dpi × 600dpi) was taken as 100%. In two-color printing with two color inks, the total amount of the inks was doubled (200%). In three-color, and four-color printing, the amount of the ink was respectively 300%, and 400%.

(Ink dyes)

[0074]

Y: C.I. Direct Yellow 86
M: C.I. Acid Red 35
C: C.I. Direct Blue 199
Bk: C.I. Food Black 2

(Ink composition 1 (standard concentration ink))

[0075]

Dye:	3 parts
Diethylene glycol:	5 parts
Polyethylene glycol:	10 parts
Water:	82 parts

(Ink composition 2 (Pale color ink 1))

[0076]

Dye:	1 parts
Diethylene glycol:	5 parts
Polyethylene glycol:	10 parts
Water:	84 parts

(Ink composition 3 (Pale color ink 2))

[0077]

Dye:	0.6 parts
Diethylene glycol:	5 parts
Polyethylene glycol:	10 parts
Water:	84.4 parts

(1: Ink absorption rate)

[0078] Printing was conducted with Ink composition 1 by means of the aforementioned ink-jet printer with ink ejection density of 5.0×10^{-3} mL/inch². Thereby the time for complete absorption of the ink was measured. The recording medium which absorbs the ink completely within one second was evaluated as "A" (good absorbency). The recording medium which absorbs the ink not completely within one second was evaluated as "C" (poor absorbency).

(2: Circularity)

[0079] Printing was conducted with Ink composition 1 by means of the aforementioned ink-jet printer with a single color ink at a density of 24×24 dots per 1 mm² (600dpi × 600dpi) (amount of the ink: 100%). The circularity of the printed dots was measured for each color according to the method described in Japanese Patent Application Laid-Open No. 61-3777. The circularity for a dot in a complete circle is taken as 1.0. The circularity becomes larger with increase of irregularity of the periphery of the dot. The circularity of 1.5 or less was evaluated to be good. When the circularity was good for the respective colors at the amount of the ink of 300%, the dot circularity was evaluated as "A" (good). When the circularity was good for the respective colors at the amount of the ink of 100%, the dot circularity was evaluated as "B" (fair). When the circularity degree was not good at the same conditions, the dot circularity was evaluated as "C" (poor).

(3. Image density)

[0080] Solid image was printed of the respective colors with Ink compositions 1 by means of the aforementioned ink-jet printer with the amount of the ink of 100% (monocolor). The transmitted image density was measured by a densitometer 310TR (X-Rite Co.).

(4. Running, bleeding, beading, crawling, and streaking)

[0081] Solid image was printed with Ink compositions 1 by means of the aforementioned ink-jet printer with the amount of the ink changing from 100% (monocolor) to 400% (four colors). The presence of the defects of running, bleeding, beading, crawling, and streaking were examined visually. When none of the defects was not found at all at the amount of ink of 400%, the recording medium was evaluated as "AA" (very good). When the defects were not found at the amount of ink of 300%, the recording medium was evaluated as "A" (good). When none of the defects was not found at the amount of ink of 100%, the recording medium is evaluated as "B" (fair). When none of the defects was found under the same conditions, the recording medium is evaluated as "C" (poor). In the present invention, the running, bleeding, beading, crawling, and streaking are defined as below. Running is a measure of image resolution of the recording medium, and denotes the phenomenon that a solid print in a prescribed area spreads or the printed area becomes larger than the originally dyed area. Bleeding denotes the phenomenon that the ink runs at the border in multi-color solid printing and the unfixed dyes comes to mix together. Beading denotes the phenomenon that the deposited ink droplets on the recording medium coalesce into a larger liquid drop in the process of absorption: visually, it is recognized as color irregularity in a visual size of a bead. Crawling denotes the occurrence of a non-dyed portion in a solid print. Streaking denotes the occurrence of streak-shaped irregularity having a breadth of the printing ink head in a solid print.

(5. Gradation, variation of tint with density)

[0082] Printing was conducted with a set of the aforementioned Ink compositions 1-3 at the ratios of the inks as shown in Table 7 by means of the aforementioned ink-jet printer. The color density was changed in about 60 steps. The printed portions were examined visually for noticeable difference in image density as discontinuity of the gradation. The gradation is evaluated as "A" (good) when no discontinuity of the tint was observed. The gradation was evaluated as "B" (fair) when two or less discontinuities of the tint were noticed. The gradation was evaluated as "C" (poor) when three or more discontinuity of the tint were noticed.

(6. Water resistance)

[0083] Solid image was printed of the respective colors with Ink compositions 1 by means of the aforementioned ink-jet printer with the amount of the ink of 100% (monocolor). The image densities of the solid images of the respective colors were measured by a densitometer 310TR (X-Rite Co.). The recording mediums were immersed in still water for three minutes, and left in the air for drying for one day. Thereafter, the image densities were measured in the same man-

ner as above. The remaining ratio of the image density of the respective colors was derived according to the equation below, and the minimum value of the ratio was taken for the respective color. The larger the minimum value, the higher the water resistance is.

$$\text{Remaining ratio (\%)} = [1 - \{(\text{Density before test} - \text{Density after test}) / (\text{Density before test})\}] \times 100$$

(Synthesis Examples 1-4)

[0084] Aluminum dodexide was prepared by the method described in U.S. Patent 4,242,271. The aluminum dodexide was hydrolyzed by the method described in U.S. Patent 4,202,870 to prepare an alumina slurry. Water was added to this alumina slurry to adjust the concentration of the alumina hydrate having the boehmite structure to 7.9% in terms of a solid content. The alumina slurry had pH of 9.4. The pH was adjusted by addition of 4% nitric acid solution to obtain fractions of solutions, and the solutions were aged under the conditions shown in Table 1 to obtain colloidal sols. The colloidal sol was spray-dried to produce powdery alumina hydrate having the boehmite structure. The alumina hydrate had the crystal structure of boehmite, and the particles were in a flat plate shape. The properties of the alumina hydrate products were measured in the aforementioned methods respectively. Table 1 shows the results.

(Production Example 1 of Ink-Receiving Layer)

[0085] A portion of 110 parts by weight of alumina hydrate A was added to 390 parts by weight of deionized water. The mixture was stirred at 1500 rpm for 30 minutes with a mixer (Portable Homomixer A510 with DS impeller blade, Satake Kagaku Kikai K.K.). While the stirring was further continued at 2500 rpm, 157 parts by weight of aqueous 10% solution of polyvinyl alcohol (Gohsenol GH17, The Nippon Synthetic Chemical Industry Co.) was added thereto. The mixture was stirred further for 30 minutes to obtain a coating liquid containing the alumina hydrate and the polymer at a weight ratio of 7/1 at a solid matter concentration of 19.1% by weight.

[0086] The coating liquid was applied onto a transparent PET film of 100 μm thick (Lumirror, Toray Industries, Inc.) by gravure coating at a coating speed of 10 m/min with simultaneous corona discharge treatment. The applied coating was dried at 120°C. Thus an ink-receiving layer was formed with the dried coating thickness of 40 μm . The properties thereof were measured according to the method shown in the above Item of "Properties of Ink-Receiving Layer". Table 2 shows the results.

(Production Examples 2-4 of Ink-Receiving Layer)

[0087] Ink-receiving layers were formed in the same manner as in "Production Example 1 of Ink-Receiving Layer" except that Alumina Hydrate A was replaced by Alumina Hydrate B in Production Example 2, by Alumina Hydrate C in Production Example 3, and by Alumina Hydrate D in Production Example 4. The evaluations were conducted in the same manner. Table 2 shows the results.

(Production Example 5 of Ink-Receiving Layer)

[0088] An ink-receiving layer was formed in the same manner as in "Production Example 1 of Ink-Receiving Layer" except that Alumina Hydrate A was replaced by silica (Mizuka Sil P-78A, Mizusawa Kagaku Kogyo K.K.; BET specific surface area: 350 m^2/g , BET pore volume: 1.53 mL/g , and average particle diameter: 2.0 μm). The properties were measured in the same manner. Table 2 shows the results.

(Example 1)

[0089] A portion of 60 parts by weight of spherical colloidal silica of methanol-dispersed type, MA-ST-M (Nissan Chemical Industries, Ltd.; particle size: 20-30 nm, solid matter concentration: 40%) was added to 300 parts by weight of ethanol. The mixture was stirred at 1500 rpm for 30 minutes with a mixer (Portable Homomixer A510 with DS impeller blade, Satake Kagaku Kikai K.K.). To this liquid dispersion, was added 34.2 parts by weight of 10% solution of alcohol-soluble nylon (Toresin MF-30, N-methoxymethylated polyamide resin, Teikoku Kagaku Sangyo K.K.) in methanol as a binder. The mixture was further stirred for 30 minutes to obtain a coating liquid containing colloidal silica and an alcohol-soluble polymer at a weight ratio (P/B) of 7/1, solid matter concentration of 7.0% by weight.

[0090] The coating liquid was applied on the ink-receiving layer of "Example 1 of Ink-Receiving Layer Production" by gravure coating at a coating rate of 20 m/min, and was dried at 120°C to form a porous layer of dried coating thickness of 5 μm . The coated sheet was cut into an A-4 size (297mm \times 210mm) to obtain a recording medium. The properties were measured according to the methods described in the above Item "Properties of Recording Medium". Table

3 shows the measurement results.

(Examples 2-7)

- 5 **[0091]** Recording mediums were produced in the same manner as in Example 1 except that the binder resin was replaced by the resin shown in Table 5 respectively. The properties were measured and evaluated in the same manner. Table 3 shows the results.

(Examples 8-11)

- 10 **[0092]** Recording mediums were produced in the same manner as in Example 1 except that the amount of addition of the binder was changed to 160 parts by weight (P/B=1.5/1) in Example 8, 80 parts by weight (P/B=3/1) in Example 9, 12 parts by weight (P/B=20/1) in Example 10, and 9.6 parts by weight (P/B=25/1) in Example 11. The properties were measured and evaluated in the same manner. Table 3 shows the results.

15 (Examples 12-17)

- 20 **[0093]** Recording mediums were produced in the same manner as in Example 1 except that the colloidal silica and the amount of addition thereof were changed as shown in Table 6. The properties were measured and evaluated in the same manner. Table 4 shows the results.

(Examples 18-20)

- 25 **[0094]** Recording mediums were produced in the same manner as in Example 1 except that the ink-receiving layer was replaced by the one produced in "Production Example 2 of Ink-Receiving Layer" in example 18, by the one produced in "Production Example 3 of Ink-Receiving Layer" in example 19, and by the one produced in "Production Example 4 of Ink-Receiving Layer" in Example 20. The measurement and evaluation were conducted in the same manner. Table 4 shows the results.

30 (Comparative Example 1)

- [0095]** A recording mediums was produced in the same manner as in Example 1 except that the ink-receiving layer was replaced by the one produced in "Production Example 5 of Ink-Receiving Layer". The measurement and evaluation were conducted in the same manner. Table 4 shows the results.

35 (Comparative Example 2)

- 40 **[0096]** A portion of 120 parts by weight of spherical colloidal silica, Snowtex 20L (Nissan Chemical Industries, Ltd.; particle size 40-50 nm, solid matter content: 20%) was added to 240 parts by weight of deionized water. The mixture was stirred at 1500 rpm for 30 minutes with a mixer (Portable Homomixer A510 with DS impeller blade, Satake Kagaku Kikai K.K.). To this liquid dispersion, was added 34.2 parts by weight of an aqueous 10% solution of silanol-modified polyvinyl alcohol (R-1130, The Nippon Synthetic Chemical Industry, Co.). The mixture was further stirred for 30 minutes to obtain a coating liquid containing colloidal silica and polyvinyl alcohol at a weight ratio (P/B) of 7/1, and a solid matter concentration of 7.0% by weight.

- 45 **[0097]** The coating liquid was applied on the ink-receiving layer of "Example 1 of Ink-Receiving Layer Production" by gravure coating at a coating rate of 10 m/min, and was dried at 120°C to form a porous layer of dried coating thickness of 5 μm. The coated sheet was cut into an A-4 size (297mm × 210mm) to obtain a recording medium. The properties were measured according to the methods described in the above Item "Properties of Recording Medium". Table 4 shows the measurement results.

50 (Comparative Example 3)

- 55 **[0098]** A recording medium was prepared in the same manner as example 1 except that the spherical colloidal silica and the amount of the addition thereof were changed to 160 parts by weight of linear colloidal silica, Snowtex OUP (Nissan Chemical Industries, Ltd.; particle size: 40-100 nm, solid matter content: 15%). The measurement and evaluation were conducted in the same manner. Table 4 shows the results.

(Comparative Example 4)

[0099] The product prepared in "Production Example 1 of Ink-Receiving Layer" without a porous layer thereon was cut into A4 size (297mm ×210mm). The physical properties were measured by the methods mentioned in "Properties of Recording Medium". Table 4 shows the measurement results.

[0100] The recording medium of the present invention absorbs ink at a high absorption rate to form high density of printed images with excellent density gradation in variable density printing without beading or streaking or the like defects of printed image. the recording medium of the present invention is excellent in surface scratch resistance, deliverability, and transparency. In the production of the recording medium of the present invention, the coating liquid is stable and the productivity is high.

Table 1

Synthesis Example No.	1	2	3	4
Alumina hydrate	A	B	C	D
Aging pH	6.6	6.6	6.5	6.5
Aging temperature (°C)	45	48	47	48
Aging period (days)	15	18	20	15
Aging apparatus	Oven	Oven	Oven	Oven
BET specific surface area (m ² /g)	200	210	235	190
Pore volume (cm ³ /g)	0.65	0.75	0.31	0.92
Average aspect ratio	5	7	9	6
Average particle diameter (nm)	21	33	40	13

Table 2

Production Example No.	1	2	3	4	5
Alumina hydrate	A	B	C	D	Silica
Crystallinity	23.2	38.5	76.8	48.3	-
Parallelization degree	2.6	1.7	3	2.1	-
BET specific surface area (m ² /g)	197	205	230	188	340
Maximum peak of pore diameter (nm)	7.5	7.6	7.1	8.1	8.5
Pore volume (PV1) (cm ³ /g)	0.64	0.73	0.30	0.86	1.51
Coating liquid dispersion state	A	A	A	A	C
Transparency	80.5	81.2	82.0	79.1	25.1
Crack	A	A	A	A	C

Table 3 (Part 1)

Example No.	1	2	3	4	5	6	7	8
Maximum peak of pore radius (nm)	7.5	7.6	7.4	7.5	7.4	7.4	7.3	6.5
Pore volume (PV2) (cm ³ /g)	0.66	0.67	0.64	0.65	0.64	0.64	0.64	0.53
PV2/PV1	1.03	1.05	1.00	1.01	1.00	1.00	1.00	0.83
Coating liquid dispersion state	A	A	A	A	A	A	A	A
State immediately after coating	A	A	A	A	A	A	A	A
Transparency	80.3	81.0	79.9	80.1	78.5	78.1	77.8	78.2
Crack	A	A	A	A	A	A	A	A
Powder-falling	A	A	A	A	A	A	A	A
Surface hardness	2H	3H	2H	2H	H	3H	2H	3H
Anti-blocking properties	A	A	A	A	A	A	A	A
Static friction coefficient	0.26	0.25	0.26	0.25	0.27	0.27	0.28	0.29
Kinetic friction coefficient	0.20	0.19	0.19	0.20	0.21	0.20	0.21	0.21
Scratch resistance	A	A	A	A	A	A	A	A
Tackiness	A	A	A	A	A	A	A	A
Ink absorption rate	A	A	A	A	A	A	A	A
Circularity	A	A	A	A	A	A	A	A
Image density	A	A	A	A	A	A	A	A
Bk	2.01	2.02	2.00	2.01	1.99	2.01	1.98	1.99
Y	1.94	1.95	1.93	1.94	1.93	1.94	1.90	1.93
M	1.95	1.95	1.94	1.96	1.93	1.94	1.91	1.93
C	1.96	1.97	1.96	1.96	1.95	1.96	1.94	1.94
Running	AA	AA	AA	AA	AA	AA	AA	AA
Bleeding	AA	AA	AA	AA	AA	AA	AA	AA
Beading	AA	AA	AA	AA	AA	AA	AA	AA
Crawling	AA	AA	AA	AA	AA	AA	AA	AA
Streaking	AA	AA	AA	AA	AA	AA	AA	AA
Gradation number	40	40	40	40	40	40	40	40
Tint change	A	A	A	A	A	A	A	A
Water resistance	98	99	98	97	97	98	98	95

(continued)

Table 3 (continued, Part 2)

Example No.	9	10	11	12	13	14	15	16
Maximum peak of pore radius (nm)	7.1	7.4	7.5	7.7	7.2	7.2	7.8	7.7
Pore volume (PV2) (cm ³ /g)	0.60	0.67	0.67	0.70	0.64	0.65	0.94	0.67
PV2/PV1	0.94	1.05	1.05	1.09	1.00	1.01	1.47	1.05
Coating liquid dispersion state	A	A	A	A	A	A	A	A
State immediately after coating	A	A	A	A	A	A	A	A
Transparency	79.5	80.5	80.4	80.1	81.0	81.0	78.5	77.6
Crack	A	A	A	A	A	A	A	A
Powder-falling	A	A	A	A	A	A	A	A
Surface hardness	3H	H	F	2H	3H	3H	H	H
Anti-blocking properties	A	A	A	A	A	A	A	A
Static friction coefficient	0.25	0.26	0.27	0.25	0.27	0.26	0.24	0.31
Kinetic friction coefficient	0.19	0.19	0.20	0.20	0.21	0.21	0.18	0.25
Scratch resistance	A	A	A	A	A	A	A	A
Tackiness	A	A	A	A	A	A	A	A
Ink absorption rate	A	A	A	A	A	A	A	A
Circularity	A	A	A	A	A	A	A	A
Image density	2.00	2.01	2.00	2.01	2.02	2.02	1.98	1.99
Bk	1.95	1.94	1.94	1.94	1.95	1.96	1.90	1.93
Y	1.94	1.96	1.94	1.94	1.95	1.94	1.90	1.93
M	1.96	1.96	1.96	1.95	1.97	1.97	1.92	1.95
C	AA	AA	AA	AA	AA	AA	AA	AA
Running	AA	AA	AA	AA	AA	AA	AA	AA
Bleeding	AA	AA	AA	AA	AA	AA	AA	AA
Beading	AA	AA	AA	AA	AA	AA	AA	AA
Crawling	AA	AA	AA	AA	AA	AA	AA	AA
Streaking	AA	AA	AA	AA	AA	AA	AA	AA
Gradation number	40	40	40	40	40	40	40	40
tint change	A	A	A	A	A	A	A	A
Water resistance	97	98	96	99	99	98	99	97
(%)								

(continued)

Table 3 (continued, Part 3)

Example No.	Comparative Example			
	1	2	3	4
Maximum peak of pore radius (nm)	8.5	1.8	7.5	7.5
Pore volume (PV2) (cm ³ /g)	1.52	0.34	0.64	0.64
PV2/PV1	1.01	0.53	1.00	-
Coating liquid dispersion state	A	A	A	-
State immediately after coating	A	C	A	-
Transparency	23.0	43.3	78.0	80.5
Crack	C	C	A	A
Powder-falling	C	C	B	A
Surface hardness	HB	B	B	B
Anti-blocking properties	A	C	A	C
Static friction coefficient	0.43	0.67	0.81	0.85
Kinetic friction coefficient	0.35	0.51	0.61	0.59
Scratch resistance	C	C	C	C
Tackiness	A	C	C	C
Ink absorption rate	A	C	A	C
Circularity	C	C	A	A
Image density	1.43	1.65	2.01	2.01
Running	1.22	1.55	1.94	1.94
Bleeding	1.18	1.54	1.94	1.94
Beading	1.20	1.59	1.95	1.95
Crawling	C	C	A	A
Streaking	AA	C	A	A
Gradation number	AA	C	A	A
Tint change	AA	C	A	A
Water resistance (%)	30	30	30	30
	C	C	B	B
	77	61	90	95

Table 4

Example No.	Resin	Manufacturer	Trade name
2	Alcohol-soluble nylon	Toray Industries, Inc.	AQ Nylon A-70
3	Polyvinylacetal	Sekisui Chemical Co.	S-LEC KS-8
4	Polyvinylbutyral	Sekisui Chemical Co.	S-LEC BX-1
5	Ethylene-vinylalcohol copolymer	Nippon Synth.Chem.Ind.Co.*	SOANOL 30T
6	Polyvinyl acetate copolymer	Shin-Etsu Chemical Co.	SMR-30L
7	Ethylcellulose	Shin-Etsu Chemical Co.	N-22G

* Nippon Synthetic Chemical Industries Co. Ltd.

Table 5

Example No.	Spherical particles	Manufacturer	Trade name	Particle diameter (nm)	Solid matter conc. (%)	Amount added (wt parts)
12	Acidic colloidal silica	Nissan Chem.*	Snowtex OL	40-50	20	120
13	Al-Modified colloidal silica	Nissan Chem.	Snowtex C	10-20	20	120
14	Acidic colloidal silica	Nissan Chem.	Snowtex O	10-20	20	120
15	Colloidal silica	Nissan Chem.	Snowtex ZL	70-100	40	60
16	Zirconia sol	Nissan Chem	NZS-30B	70	30	80
17	Styrene-acryl copolymer resin	Hoechst **	Moviny 790***	100	40	60

* Nissan Chemical Industries, Ltd.

** Hoechst Synthesis Co.

*** Organic filler with no film formability, Tg=220°C

Table 6

5	Ratio of Inks Used								
	Standard color ink	Pale color ink 1	Pale color ink 2	Standard color ink	Pale color ink 1	Pale color ink 2	Standard color ink	Pale color ink 1	Pale color ink 2
10	10	0	0	5	0	5	1	7	2
	9	1	0	4	4	2	2	2	6
	9	0	1	4	3	3	1	6	3
	8	2	0	3	7	0	2	1	7
15	8	1	1	4	2	4	0	10	0
	8	0	2	3	6	1	1	5	4
	7	3	0	4	1	5	2	0	8
	7	2	1	3	5	2	0	9	1
20	7	1	2	4	0	6	1	4	5
	7	0	3	3	4	3	0	8	2
	6	4	0	2	8	0	1	3	6
	6	3	1	3	3	4	0	7	3
25	6	2	2	2	7	1	1	2	7
	6	1	3	3	2	5	0	6	4
	5	5	0	2	6	2	1	1	8
	6	0	4	3	1	6	0	5	5
30	5	4	1	2	5	3	1	0	9
	5	3	2	3	0	7	0	4	6
	5	2	3	1	9	0	0	3	7
	4	6	0	2	4	4	0	2	8
35	5	1	4	1	8	1	0	1	9
	4	5	1	2	3	5	0	0	10
	(Ten parts of inks in total)								
40									

[0101] A recording medium comprising at least a base member, an ink-receiving layer containing alumina hydrate of a boehmite structure formed on the base member, and a porous layer containing particles and an alcohol-soluble organic polymer resin formed further on the ink-receiving layer.

Claims

1. A recording medium comprising at least a base member, an ink-receiving layer containing alumina hydrate of a boehmite structure formed on the base member, and a porous layer containing particles and an alcohol-soluble organic polymer resin formed further on the ink-receiving layer.
2. The recording medium according to claim 1, wherein the porous layer is formed by coating a liquid dispersion containing the particles and the organic polymer resin, the solvent of the liquid dispersion containing an alcohol at a content not less than 30% by weight.
3. The recording medium according to claim 1, wherein the particles have a particle diameter ranging from 10 nm to 100 nm.

4. The recording medium according to claim 1, wherein the particles and the organic polymer resin are mixed at a ratio ranging from 1:1 to 30:1 by weight.
- 5 5. The recording medium according to claim 1, wherein the alumina hydrate of the boehmite structure has an average aspect ratio ranging from 3 to 10.
6. The recording medium according to claim 1, wherein the alumina hydrate contained in the recording medium has a crystallinity ranging from 15 to 80.
- 10 7. The recording medium according to claim 1, wherein the parallelization degree between the fine crystals of the alumina hydrate of the boehmite structure and the plane direction of the ink-receiving layer is not less than 1.5.
8. The recording medium according to claim 1, wherein the alumina hydrate of the boehmite structure has a BET specific surface area ranging from 40 to 500 m²/g.
- 15 9. The recording medium according to claim 1, wherein the alumina hydrate of the boehmite structure has a pore volume ranging from 0.1 to 1.0 cm³/g.
10. The recording medium according to claim 1, wherein the ink-receiving layer contains a binder.
- 20 11. The recording medium according to claim 1, wherein the alumina hydrate and the binder are mixed at a mixing ratio ranging from 1:1 to 30:1 by weight.
12. The recording medium according to claim 1, wherein the ink-receiving layer has a BET specific surface area ranging from 40 to 450 m²/g.
- 25 13. The recording medium according to claim 1, wherein the ink-receiving layer has a pore volume ranging from 0.1 to 1.0 cm³/g.
- 30 14. The recording medium according to claim 1, wherein the ink-receiving layer has the maximum peak of pore radius distribution within the range from 2.0 to 20.0 nm.
15. The recording medium according to claim 1, wherein the pore volume of the total layers of the porous layer and the ink-receiving layer ranges from 0.1 to 1.0 cm³/g.
- 35 16. The recording medium according to claim 1, wherein the ratio (PV2/PV1) of the overall pore volume (PV2) of the ink-receiving layer and the porous layer to the pore volume (PV1) of the ink-receiving layer ranges from 0.6 to 1.5.
17. The recording medium according to claim 1, wherein the pore radius distribution of the total layers of the porous layer and the ink-receiving layer has a maximum peak in the range from 2.0 to 20.0 nm.
- 40 18. The recording medium according to claim 1, wherein the ink applied at a resolution of 600dpi×600dpi and a density of 5.0×10⁻³ ml/inch² is absorbed within one second.
- 45 19. A process for forming an image, comprising ejecting ink droplets through a fine nozzle onto the recording medium set forth in any of claims 1 to 18.
20. A process according to claim 19, wherein the ink is ejected by exerting a thermal energy to the ink.
- 50 21. A process for producing a recording medium having an ink-receiving layer formed on a base member, and a porous layer formed thereon, comprising the steps of applying a liquid dispersion containing an alumina hydrate of a boehmite structure and a binder on the base member followed by drying to form at least one ink-receiving layer, and further applying another liquid dispersion containing an alcohol-soluble organic polymer resin dissolved in an alcohol-containing solvent and a particulate material followed by drying to form a porous layer.
- 55



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 12 6018

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	EP 0 705 710 A (ASAHI GLASS CO LTD) 10 April 1996 (1996-04-10) * examples *	1,3,4,19	B41M5/00
X	EP 0 756 941 A (ASAHI GLASS CO LTD) 5 February 1997 (1997-02-05) * examples *	1,3,4,19	
D,X	EP 0 634 287 A (ASAHI GLASS CO LTD) 18 January 1995 (1995-01-18) * example 1 *	1,19	
P,X	EP 0 891 873 A (ASAHI GLASS CO LTD) 20 January 1999 (1999-01-20) * examples *	1,3,19	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 7) B41M
Place of search THE HAGUE		Date of completion of the search 24 February 2000	Examiner Heywood, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 12 6018

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24-02-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0705710 A	10-04-1996	JP 8072388 A US 5985076 A	19-03-1996 16-11-1999
EP 0756941 A	05-02-1997	JP 9104166 A	22-04-1997
EP 0634287 A	18-01-1995	DE 69402003 D DE 69402003 T JP 7076162 A US 5463178 A	17-04-1997 19-06-1997 20-03-1995 31-10-1995
EP 0891873 A	20-01-1999	JP 11078225 A	23-03-1999