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(54) **TREATMENT LIQUID COMPOSITION FOR INK JET PIGMENT TEXTILE PRINTING,
TREATMENT LIQUID COMPOSITION SET FOR INK JET PIGMENT TEXTILE PRINTING, AND
INK JET TEXTILE PRINTING METHOD**

(57) A treatment liquid composition for ink jet pigment textile printing according to the invention is used by being attached to a fabric and contains a cationic compound, a nonionic fluorine-based surfactant, a resin particle, and water.

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Description**BACKGROUND**

5 1. Technical Field

[0001] The present invention relates to a treatment liquid composition for ink jet pigment textile printing, a treatment liquid composition set for ink jet pigment textile printing, and an ink jet pigment textile printing method.

10 2. Related Art

[0002] It is known for dyeing (textile printing) of fabrics to be performed using an ink jet recording method. Other known recording methods for fabrics (textiles or nonwoven fabrics) include screen textile printing, roller textile printing, and the like. However, the use of ink jet recording is advantageous for producing a wide-variety of small production lots, immediate printability, and the like, and therefore various studies have been conducted.

[0003] In the field of textile printing ink jet recording, investigations have been carried out on a so-called ink jet pigment textile printing method (hereinafter also simply referred to as "pigment textile printing") including textile printing a fabric by compounding a pigment and a fixing resin with an ink composition (hereinafter also simply referred to as "ink"). In pigment textile printing, the color developability is sometimes decreased due to the fact that the ink permeates into the fabric, and thus improvements in color developability are needed. This is particularly the case for polyester or polyester mixed fabrics, where the ink is more likely to sink into the fabric and it is therefore difficult to obtain good color development.

[0004] It is known to use a treatment liquid, such as a pretreatment agent, in pigment textile printing to physically fix the pigment to the surface of fibers of the fabric for the purpose of improving the color developability of a printed textile to be obtained (for example, see JP-A-2008-266853).

[0005] However, in ink jet pigment textile printing methods using a treatment liquid and a pigment textile printing ink jet ink composition, a further improvement of the color developability are necessary.

SUMMARY

[0006] An advantage of some aspects of the invention is to provide a treatment liquid composition for ink jet pigment textile printing, a treatment liquid composition set for ink jet pigment textile printing, and an ink jet pigment textile printing method which provide a printed textile having excellent color developability.

[0007] The invention has been made in order to solve at least partially the above-described problems and can be realized as the following items.

35 Item 1

[0008] A treatment liquid composition for ink jet pigment textile printing according to a first aspect of the invention is a treatment liquid composition for attachment to a fabric in ink jet pigment textile printing and which contains a cationic compound, a nonionic fluorine-based surfactant, a resin particle, and water.

[0009] Using the treatment liquid composition of Item 1, permeation of an ink into the fabric is suppressed. The nonionic fluorine-based surfactant attached to the fabric holds the ink on the surface of the fabric and thus the sinking of the pigment into the fabric is suppressed. Moreover, because the surfactant is nonionic, unevenness in color development hardly occurs. Thus, according to Item 1, due to the fact that the treatment liquid composition for ink jet pigment textile printing attached to the fabric contains the nonionic fluorine-based surfactant, a printed textile having excellent color developability is obtained.

Item 2

[0010] In the treatment liquid composition of Item 1 above, the fabric can comprise polyester or polyester mixed yarn.

[0011] According to Item 2, a printed textile excellent in color developability is obtained even in pigment textile printing to a fabric comprising polyester or polyester mixed yarn in which an ink easily sinks downward because the nonionic fluorine-based surfactant holds the ink on the fabric surface.

55 Item 3

[0012] In the treatment liquid composition of the invention, the cationic compound can be a polyvalent metal salt, an organic acid, or a cationic resin.

[0013] Because the cationic compound is a polyvalent metal salt or an organic acid, unevenness hardly occurs in color development, and thus a printed textile having excellent color developability is obtained.

Item 4

[0014] In the treatment liquid composition of the invention, the cationic compound can contain either calcium nitrate or calcium chloride.

[0015] When the cationic compound is either calcium nitrate or calcium chloride, unevenness in color development hardly occurs, and thus printed textile with excellent color developability is obtained.

Item 5

[0016] In the treatment liquid composition of the invention, the nonionic fluorine-based surfactant can have an HLB value within the range of 6 or more and 15 or less.

[0017] When the HLB value of the nonionic fluorine-based surfactant is within the range of 6 or more and 15 or less, permeation of an ink into the fabric is suppressed, and thus a printed textile having improved color developability is obtained.

Item 6

[0018] In the treatment liquid composition of the invention, the nonionic fluorine-based surfactant may comprise a polyoxyethylene group and an alkyl fluoride group.

[0019] When the nonionic fluorine-based surfactant comprises a polyoxyethylene group, which is a hydrophilic group, and an alkyl fluoride group, which is a hydrophobic group, permeation of an ink into the fabric and sinking of the pigment into the fabric are further suppressed, so that a printed textile having improved color developability is obtained.

Item 7

[0020] In the treatment liquid composition of the invention, the resin particle can be a nonionic or cationic resin particle.

[0021] When the resin particle is a nonionic resin particle, a printed textile having excellent color developability and rubbing fastness is obtained, particularly in textile printing to cotton. Moreover, according to Item 7, because the resin particle is a cationic resin particle, a printed textile having excellent color developability and rubbing fastness is obtained in textile printing, particularly in textile printing to a fabric comprising polyester or polyester mixed yarn.

Item 8

[0022] An ink jet pigment textile printing set according to a second aspect of the invention contains the treatment liquid composition for ink jet pigment textile printing according to the first aspect as set out in any one of Items 1 to 7, and a pigment textile printing ink jet ink composition comprising a pigment, a resin particle, and water.

[0023] The pigment textile printing ink jet ink composition set of Item 8 provides a printed textile having excellent color developability, particularly when using a two-layer printing method comprising performing pigment textile printing using the pigment textile printing ink jet ink composition, and further performing pigment textile printing using an ink containing a chromatic color pigment.

Item 9

[0024] In the pigment textile printing ink jet ink composition set of the invention, the resin particle contained in the pigment textile printing ink jet ink composition may comprise a polycarbonate-based urethane resin.

[0025] There is a tendency for the printed textile obtained using a pigment textile printing ink jet ink composition set of the invention to have poor rubbing fastness because of the presence of the nonionic fluorine-based surfactant. However, by the use of polycarbonate-based urethane resin particles as the resin particles, the pigment is likely to be fixed to the surface of a fabric and, even when the nonionic fluorine-based surfactant is used, a printed textile having excellent color developability and rubbing fastness is obtained.

Item 10

[0026] In the pigment textile printing ink jet ink composition set of the invention, the pigment textile printing ink jet ink composition can further contain a fluorine-based surfactant.

[0027] When the pigment textile printing ink jet ink composition further contains a fluorine-based surfactant, the permeability of an ink into the fabric is further controlled, and thus a printed textile having excellent color developability is obtained.

Item 11

[0028] An ink jet pigment textile printing method according to a third aspect of the invention includes attaching a pigment textile printing ink jet ink composition to a region where the treatment liquid composition for ink jet pigment textile printing according to any one of Items 1 to 7 is attached by an ink jet method.

[0029] According to Item 11, permeation of the ink into a fabric is suppressed by attaching the pigment textile printing ink jet ink composition onto the treatment liquid composition of the first aspect of the invention. Moreover, ink components are coagulated by a reaction or an interaction of the cationic compound of the treatment liquid composition with the ink components. Thus, a printed textile having excellent color development properties is obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] The invention will be described with reference to the accompanying drawing, wherein like numbers reference like elements.

[0031] Figure is a schematic perspective view of a textile printing apparatus performing an ink jet pigment textile printing method according to the invention.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0032] Hereinafter, some embodiments of the invention are described. The embodiments described below describe examples of the invention. The invention is not limited to the following embodiments and also includes various modifications to be implemented without altering the gist of the invention. All the configurations described below are not necessarily indispensable configurations of the invention.

[0033] Hereinafter, with respect to a treatment liquid composition for ink jet pigment textile printing, a treatment liquid composition set for ink jet pigment textile printing, and an ink jet pigment textile printing method according to the invention, the configuration of a textile printing apparatus capable of implementing the same, a pigment textile printing ink jet ink composition (hereinafter also referred to as "pigment textile printing ink", "ink composition", or "ink") configuring the treatment liquid composition set for ink jet pigment textile printing (hereinafter also referred to as "treatment liquid set") containing the treatment liquid composition for ink jet pigment textile printing together with the treatment liquid composition for ink jet pigment textile printing, the treatment liquid composition for ink jet pigment textile printing (hereinafter also referred to as "treatment liquid"), the treatment liquid composition set for ink jet pigment textile printing, a fabric to which the ink jet pigment textile printing method is performed, and the ink jet pigment textile printing method are described in detail in this order.

1. Textile printing apparatus

[0034] First, an example of a textile printing apparatus to be used in the invention is described with reference to the drawing. The textile printing apparatus to be used in the invention is not limited to the following aspect.

[0035] The textile printing apparatus to be used in this invention is described by way of example with reference to taking an on-carriage type printer in which an ink cartridge is mounted in a carriage. However, the textile printing apparatus is not limited to an on-carriage type printer and may be an off-carriage type printer in which an ink cartridge is not mounted in a carriage and is fixed to the outside.

[0036] the printer described below is a serial printer in which a print head is mounted in a carriage moving in the predetermined direction and which discharges droplets onto a recording medium by the movement of a head in connection with the movement of the carriage. However, textile printing apparatus for use in the invention is not limited to serial printers and may be a line printer in which a head is formed to be larger than the width of a recording medium and which discharges droplets onto a recording medium without the movement of a print head.

[0037] In a figure used for the following description, the scale of each member is changed as appropriate so that each member can be recognized.

[0038] The textile printing apparatus may be, for example, an ink jet printer (hereinafter also referred to as "printer") mounted with an ink jet head illustrated in the Figure. As illustrated in the Figure, a printer 1 has a carriage 4 which is mounted with an ink jet head 2 and to which an ink cartridge 3 is detachably attached, a platen 5 which is disposed below the ink jet head 2 and to which a fabric M which is a recording medium is transported, a heating mechanism 6 for heating the fabric M, a carriage moving mechanism 7 causing the carriage 4 to move in the medium width direction of

the fabric M, and a medium feeding mechanism 8 transporting the fabric M in the medium feeding direction. Moreover, the printer 1 has a control device CONT controlling an operation of the whole printer 1. The medium width direction is a main scanning direction (head scanning direction). The medium feeding direction is a subscanning direction (direction orthogonal to the main scanning direction).

[0039] The ink jet head 2 is a unit for attaching an ink to the fabric M and is provided with a plurality of nozzles (not illustrated) for discharging the ink onto a surface of the fabric M. The plurality of nozzles is arranged in an array shape, and thus a nozzle surface is formed on the nozzle plate surface.

[0040] Examples of systems of discharging an ink from nozzles include, for example, a system of applying a strong electric field between the nozzles and an accelerating electrode placed in front of the nozzles to continuously discharge an ink in the form of droplets from the nozzles and discharging the ink droplets corresponding to a recording information signal while the ink droplets are flying between deflecting electrodes (electrostatic suction system); a system of applying a pressure to a treatment liquid with a small pump to mechanically vibrate nozzles with a quartz oscillator or the like to thereby forcibly discharge ink droplets; a system of simultaneously applying a pressure and a recording information signal to an ink with a piezoelectric element to discharge and record ink droplets (piezoelectric system); a system of heating and foaming an ink with a microelectrode according to a recording information signal to discharge and record ink droplets (thermal jet system); and the like.

[0041] The ink jet head 2 may be either a line type ink jet head or a serial type ink jet head, although a serial type ink jet head is used in this embodiment.

[0042] Herein, the textile printing apparatus provided with the serial type ink jet head performs recording by performing scanning (path) of discharging an ink while moving an ink jet head for recording relatively to a recording medium several times. Specific examples of serial type ink jet heads include one in which an ink jet head is mounted in a carriage moving in the width direction of a recording medium (direction crossing the transporting direction of the recording medium) and which discharges droplets onto the recording medium by the movement of the ink jet head in connection with the movement of the carriage.

[0043] On the other hand, a textile printing apparatus provided with a line type ink jet head performs recording by performing scanning (path) of discharging an ink while moving the ink jet head relatively to a recording medium once. Specific examples of line type ink jet heads include one in which the ink jet head is formed to be larger than the width of a recording medium and which discharges droplets onto the recording medium without the movement of the ink jet head.

[0044] The ink cartridge 3 supplying an ink to the ink jet head 2 contains four independent cartridges. Each of the four cartridges may be filled with a different kind of ink. The ink cartridge 3 is detachably attached to the ink jet head 2. In the example of the Figure, the number of the cartridges is four but any desired number of cartridges can be mounted on the ink jet head 2.

[0045] The carriage 4 is supported with a guide rod 9 which is a support member installed in the main scanning direction. The carriage 4 moves in the main scanning direction along the guide rod 9 by the carriage moving mechanism 7. Although the example of the Figure illustrates the carriage 4 moving in the main scanning direction, the invention is not limited thereto and the carriage 4 may move in the subscanning direction in addition to the movement in the main scanning direction.

[0046] The installation position of the heating mechanism 6 is not particularly limited insofar as the heating mechanism 6 is provided at a position where the fabric M can be heated. In the example of Figure, the heating mechanism 6 is disposed at a position which is located on the platen 5 and in which the heating mechanism 6 faces the ink jet head 2. Thus, when the heating mechanism 6 is disposed at the position where the heating mechanism 6 faces the ink jet head 2, the attachment position of droplets in the fabric M can be heated, and therefore the droplets attached to the fabric M can be efficiently dried.

[0047] Examples of suitable heating mechanisms 6 include a print heater mechanism of bringing the fabric M into contact with a heat source for heating, a mechanism of emitting infrared rays, microwaves (electromagnetic waves having a maximum wavelength around 2,450 MHz), or the like, a drier mechanism spraying warm air, and the like.

[0048] The heating of the fabric M by the heating mechanism 6 is performed before or when the droplets discharged from the nozzles of the ink jet head 2 are attached to the fabric M. The control (for example, the timing of performing the heating, heating temperature, heating time, and the like) of the conditions for the heating is performed by the control device CONT.

[0049] The heating of the fabric M by the heating mechanism 6 is performed so that the fabric M holds the temperature range of 35°C or more and 65°C or less from the viewpoint of an improvement of the wettability and spreadability, permeability, and drying property, discharge stability, and the like of an ink. Herein, the temperature for heating the fabric M means the temperature of the surface of the recording surface of the fabric M in heating.

[0050] The printer 1 may further have a second heating mechanism which is not illustrated besides the heating mechanism 6. In that case, the second heating mechanism is disposed on the downstream side in the transporting direction of the fabric M relative to the heating mechanism 6. The second heating mechanism heats the fabric M after the fabric M is heated by the heating mechanism 6, i.e., after the droplets discharged from the nozzles are attached to the fabric

M. Thus, the drying property of the droplets of the ink attached to the fabric M is improved. For the second heating mechanism, any one of the mechanisms described for the heating mechanism 6 (for example, drier mechanism, heat press machine, and the like) is usable. The heating by the second heating mechanism is preferably performed so that the fabric M holds the temperature range of 100°C or more and 200°C or less.

[0051] A linear encoder 10 detects the position in the main scanning direction of the carriage 4 by a signal. The detected signal is transmitted to the control device CONT as position information. The control device CONT recognizes the scanning position of the recording head 2 based on the position information from the linear encoder 10 to control a recording operation (discharge operation) by the recording head 2 and the like. Moreover, the control device CONT is configured so as to be able to variably control the movement speed of the carriage 4.

2. Pigment textile printing ink jet ink composition

[0052] The pigment textile printing ink jet ink composition to be used in the invention comprises a pigment, resin particles, a nonionic fluorine-based surfactant, and water and is used by being attached to a fabric. Hereinafter, the pigment textile printing ink jet ink composition is described.

[0053] The pigment textile printing ink jet ink composition to be used in the invention may be comprised in an ink jet pigment textile printing set together with the treatment liquid composition for ink jet pigment textile printing described below. When the pigment textile printing ink jet ink composition set comprises two or more of the pigment textile printing ink jet ink compositions, it is preferable that one of the pigment textile printing ink jet ink compositions is a white pigment textile printing ink jet ink composition containing a white pigment and each of the other pigment textile printing ink jet ink compositions is a chromatic color pigment textile printing ink jet ink composition containing a chromatic color pigment. In this case, the ink jet pigment textile printing method may be a two-layer printing in which color printing is performed on a white base as described later.

2.1. Pigment

[0054] The pigment textile printing ink jet ink composition to be used in the invention contains a pigment. Due to the attachment of the pigment to a fabric, the fabric is textile printed, so that a printed textile (printed matter) is formed.

[0055] The pigment may be either an organic pigment or an inorganic pigments and a pigment of any color may be used. When the ink jet pigment textile printing set contains a plurality of pigment textile printing ink jet ink compositions, it is preferable that one of the plurality of pigment textile printing ink jet ink compositions contains a white pigment as the pigment and the other pigment textile printing ink jet ink compositions contain chromatic color pigments.

[0056] Examples of white pigments include, but are not limited to the following substances, white inorganic pigments, such as titanium oxide, zinc oxide, zinc sulfide, antimony oxide, and zirconium dioxide, and the like. In addition to the white inorganic pigments, white organic pigments, such as white hollow resin particles and polymer particles, are also usable.

[0057] Examples of the Color Index (C.I.) of the white pigment include, but are not limited to the following substances, C.I. Pigment White 1 (basic lead carbonate), 4 (zinc oxide), 5 (mixture of zinc sulfide and barium sulfate), 6 (titanium oxide), 6:1 (titanium oxide containing other metal oxides), 7 (zinc sulfide), 18 (calcium carbonate), 19 (clay), 20 (mica titanium), 21 (barium sulfate), 22 (natural barium sulfate), 23 (gloss white), 24 (alumina white), 25 (gypsum), 26 (magnesium oxide-silicon oxide), 27 (silica), 28 (anhydrous calcium silicate), and the like, for example. Among the above, titanium oxide is preferable as the white pigment because the color developability, the concealing properties, and the visibility (brightness) are excellent and a good dispersion particle size is obtained.

[0058] Among the titanium oxides, a rutile type titanium oxide common as the white pigment is preferable. The rutile type titanium oxide may be produced by oneself or may be a commercially available substance. Examples of industrial production methods when the rutile type titanium oxide (powdered) is produced by oneself include known sulfuric acid method and chlorine method. Examples of commercially-available items of the rutile type titanium oxide include, for example, rutile types, such as Tipaque (Registered Trademark) CR-60-2, CR-67, R-980, R-780, R-850, R-980, R-630, R-670, and PF-736 (all Trade Names, manufactured by Ishihara Sangyo Kaisha, Ltd.).

[0059] Suitable chromatic color pigments include pigments other than the white pigments mentioned above. Examples of such pigments include, although are not limited to, the following substances: azo-based, phthalocyanine-based, dye-based, condensed polycyclic-based, nitro-based, and nitroso-based organic pigments (Brilliant Carmine 6B, Lake Red C, Watchung Red, Disazo Yellow, Hansa Yellow, Phthalocyanine Blue, Phthalocyanine Green, Alkali Blue, Aniline Black, and the like), metals, such as cobalt, iron, chromium, copper, zinc, lead, titanium, vanadium, manganese, and nickel, metal oxides and sulfides, carbon blacks (C.I. Pigment Black 7), such as furnace carbon black, lamp black, acetylene black, and channel black, and further inorganic pigments, such as ocher, ultramarine, and Prussian blue.

[0060] In more detail, examples of carbon black to be used as black pigments include No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100, No. 2200B, and the like (all manufactured by Mitsubishi Chemical

Corporation), Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, Raven 700, and the like (all manufactured by Columbian Carbon Japan Ltd.), Regal 400R, Regal 330R, Regal 660R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, Monarch 1400, and the like (all manufactured by Cabot Corporation company), Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, Printex 35, Printex U, Printex V, Printex 140U, Special Black 6, Special Black 5, Special Black 4A, and Special Black 4 (all manufactured by Degussa), and the like.

[0061] Examples of yellow pigments include C.I. Pigment Yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 16, 17, 24, 34, 35, 37, 53, 55, 65, 73, 74, 75, 81, 83, 93, 94, 95, 97, 98, 99, 108, 109, 110, 113, 114, 117, 120, 124, 128, 129, 133, 138, 139, 147, 151, 153, 154, 167, 172, and 180, and the like.

[0062] Examples of magenta pigments include C.I. Pigment Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 40, 41, 42, 48 (Ca), 48 (Mn), 57 (Ca), 57:1, 88, 112, 114, 122, 123, 144, 146, 149, 150, 166, 168, 170, 171, 175, 176, 177, 178, 179, 184, 185, 187, 202, 209, 219, 224, and 245, C.I. Pigment Violet 19, 23, 32, 33, 36, 38, 43 and 50, and the like.

[0063] Examples of cyan pigments include C.I. Pigment Blue 1, 2, 3, 15, 15:1, 15:2, 15:3, 15:34, 15:4, 16, 18, 22, 25, 60, 65, and 66, C.I. Vat Blue 4 and 60, and the like.

[0064] Examples of pigments other than the black, yellow, magenta, and cyan pigments include, for example, C.I. Pigment Green 7 and 10, C.I. Pigment Brown 3, 5, 25, and 26, C.I. Pigment Orange 1, 2, 5, 7, 13, 14, 15, 16, 24, 34, 36, 38, 40, 43, and 63, and the like.

[0065] The pigments mentioned above may be used alone or two or more thereof may be used in combination.

[0066] The content of the pigment contained in the pigment textile printing ink jet ink composition to be used in the invention varies depending on the pigment type to be used and is preferably 1% by mass or more and 30% by mass or less, more preferably 3% by mass or more and 15% by mass or less, and still more preferably 5% by mass or more and 13% by mass or less based on the total mass (100% by mass) of the ink from the viewpoint of securing good color developability. Among the above, when the titanium oxide is used as the pigment contained in the ink, the content of the titanium oxide is preferably 3% by mass or more and 25% by mass or less and more preferably 5% by mass or more and 20% by mass or less based on the total mass of the ink because the titanium oxide is hard to precipitate and has excellent concealing properties and color reproducibility on a fabric having low brightness. The content is more preferably 7% by mass or more and 15% by mass or less and still more preferably 12% by mass or less.

[0067] In preparing the pigment textile printing ink jet ink composition, a pigment dispersion liquid in which a pigment is dispersed beforehand may be prepared. This pigment dispersion liquid may be added to and mixed with a dispersion liquid of another material. Examples of methods for obtaining a pigment dispersion liquid include dispersing a self-dispersible pigment in a dispersant without using a dispersant; dispersing a pigment in a dispersant using a polymer dispersant (resin dispersant); dispersing a surface-treated pigment in a dispersant, and the like. Resin dispersant

[0068] Examples of the resin dispersant include, but are not particularly limited to, polyvinyl alcohols, polyvinyl pyrrolidones, polyacrylic acids, an acrylic acid-acryl nitrile copolymer, a vinyl acetate-acrylic acid ester copolymer, an acrylic acid-acrylic acid ester copolymer, a styrene-acrylic acid copolymer, a styrene-methacrylic acid copolymer, a styrene-methacrylic acid-acrylic acid ester copolymer, a styrene- α -methyl styrene-acrylic acid copolymer, a styrene- α -methyl styrene-acrylic acid-acrylic acid ester copolymer, a styrene-maleic acid copolymer, a styrene-maleic anhydride copolymer, a vinyl naphthalene-acrylic acid copolymer, a vinyl naphthalene-maleic acid copolymer, a vinyl acetate-maleic acid ester copolymer, a vinyl acetate-crotonic acid copolymer, a vinyl acetate-acrylic acid copolymer, and the like and salts thereof, for example. Among the above, copolymers of monomers having hydrophobic functional groups and monomers having hydrophilic functional groups and polymers containing monomers having both hydrophobic functional groups and hydrophilic functional groups are particularly preferable. As the form of the copolymer, the copolymer can be used in any form of a random copolymer, a block copolymer, an alternating copolymer, and a graft copolymer.

[0069] As the resin dispersant, commercially-available products may also be used. Specific examples of such products include Joncryl 67 (Weight average molecular weight: 12,500, Acid value: 213), Joncryl 678 (Weight average molecular weight: 8,500, Acid value: 215), Joncryl 586 (Weight average molecular weight: 4,600, Acid value: 108), Joncryl 611 (Weight average molecular weight: 8,100, Acid value: 53), Joncryl 680 (Weight average molecular weight: 4,900, Acid value: 215), Joncryl 682 (Weight average molecular weight: 1,700, Acid value: 238), Joncryl 683 (Weight average molecular weight: 8,000, Acid value: 160), Joncryl 690 (Weight average molecular weight: 16,500, Acid value: 240) (all Trade Name, manufactured by Basf Japan, Inc.), and the like.

2.2. Resin particles

[0070] The pigment textile printing ink jet ink composition to be used in the invention contains resin particles. The resin particles improve the fixability of an image to be formed of the ink composition by forming a resin coating film, and thus can improve the washing fastness and the rubbing fastness of the image. The resin particles, may be provided in an emulsion state or in a solution state. However, emulsion state resins are preferable from the viewpoint of suppressing

an increase in the viscosity of the ink.

[0071] Suitable resins for the resin particles include: acrylic resin, styrene acrylic resin, fluorene-based resin, urethane-based resin, polyolefin-based resin, rosin-modified resin, terpene-based resin, polyester-based resin, polyamide-based resin, epoxy-based resin, vinyl chloride-based resin, a vinyl chloride-vinyl acetate copolymer, ethylene vinyl acetate-based resin, and the like. The resins may be used alone or two or more kinds thereof may be used in combination.

[0072] Among the resins listed above, it is preferable to use at least one kind selected from a urethane-based resin and an acrylic resin because the degree of freedom in design is high, and thus desired physical properties are easily obtained. Urethane-based resins are more preferably used from the viewpoint of improving the rubbing fastness. The urethane-based resin may be any one of: a polyether type containing an ether bond, a polyester type containing an ester bond, a polycarbonate type containing a carbonate bond, and the like. The elongation at fracture point and the 100% modulus when a urethane-based resin having a crosslinkable group is crosslinked (crosslinked object) can be adjusted by changing the density of the crosslinking point and the nature of the main chain. Among the above examples, it is more preferable to use a urethane-based resin comprising a crosslinkable group and a polycarbonate-based or a polyether-based skeleton in order to ensure that the balance between the elongation at fracture point and the 100% modulus is good and that the rubbing fastness of an image and the texture of a printed textile are improved. A polycarbonate-based urethane resin having a polycarbonate-based skeleton is particularly preferable because the polycarbonate-based urethane resin tends to be able to improve the rubbing fastness. In particular, because the pigment textile printing ink jet ink composition according to the invention contains a nonionic fluorine-based surfactant, there is a tendency for the rubbing fastness of a printed textile obtained to be poor. However, by the use of polycarbonate-based urethane resin particles as the resin particles, the pigment is likely to be fixed to the surface of a fabric and, even when the nonionic fluorine-based surfactant is used, a printed textile with excellent color developability and rubbing fastness is obtained.

[0073] The urethane resin is preferably a polycarbonate-based urethane resin or the like and comprises a urethane resin containing a crosslinkable group, for example. Suitable crosslinkable groups include an isocyanate group and a silanol group. Preferably, the crosslinkable group is one in which an isocyanate group is chemically protected (capping or blocking) (blocked isocyanate group). The blocked isocyanate group is deprotected by being heated to be activated to form a bond (for example, urethane bond, urea bond, allophanate bond, and the like).

[0074] It is preferable that the urethane-based resin having a crosslinkable group preferably has three or more crosslinkable groups in one molecule. In such a case, a crosslinking structure is formed by the reaction of the crosslinkable groups. In this specification, "urethane-based resin" refers to resins comprising a urethane bond, a urea bond, an allophanate bond, and the like formed by the reaction of the isocyanate group with the other reactive groups (for example, a hydroxyl group, an amino group, a urethane bond group, a carboxyl group, and the like). Therefore, a urea resin is a "urethane-based resin" for the purposes of this specification, for example. The urethane-based resin is preferably a compound having a urethane bond obtained by the reaction of a compound having an isocyanate group and a compound having a hydroxyl group.

[0075] The blocked isocyanate (chemically protected isocyanate) contains a latent isocyanate group obtained by blocking the isocyanate group by a blocking agent and can be obtained by reacting a polyisocyanate compound with a blocking agent.

[0076] Examples of the polyisocyanate compound include polyisocyanate monomers, polyisocyanate derivatives, and the like. Examples of polyisocyanate monomers include polyisocyanates, such as aromatic polyisocyanates, araliphatic polyisocyanates, aliphatic polyisocyanates, and alicyclic polyisocyanates, and the like. The polyisocyanate monomers can be used alone or in combination of two or more kinds thereof.

[0077] Examples of the polyisocyanate derivatives include polymers of the polyisocyanate monomers mentioned above (for example, dimers, trimers (for example, an isocyanurate modified substance and an iminooxadiazine dione modified substance), pentamers, heptamers, and the like), and allophanate modified substances (for example, allophanate modified substances generated by the reaction of the polyisocyanate monomers mentioned above with low molecular weight polyols described later), polyol modified substances (for example, polyol modified substances (alcohol adduct) and the like generated by the reaction of polyisocyanate monomers with low molecular weight polyols described later), biuret modified substances (for example, biuret modified substances and the like generated by the reaction of the polyisocyanate monomers mentioned above with water or amines), urea modified substances (for example, urea modified substances and the like generated by the reaction of the polyisocyanate monomers mentioned above with diamines), oxadiazine trione modified substances (for example, oxadiazine trione and the like generated by the reaction of the polyisocyanate monomers mentioned above and carbon dioxides), carbodiimide modified substances (carbodiimide modified substances and the like generated by a decarboxylation condensation reaction of the polyisocyanate monomers mentioned above), uretdione modified substances, uretonimine modified substances, and the like, for example.

[0078] When two or more of the polyisocyanate compounds are used in combination, two or more polyisocyanate compounds may be simultaneously reacted or blocked isocyanates obtained individually using the polyisocyanate compounds may be mixed to produce a blocked isocyanate.

[0079] The blocking agent blocks and inactivates the isocyanate group and can be removed such that the isocyanate

group is regenerated. The blocking agent also has a catalytic action of activating the isocyanate group in a state where the isocyanate group is blocked or deblocked.

[0080] Examples of the blocking agent include imidazole-based compounds, imidazoline-based compounds, pyrimidine-based compounds, guanidine-based compounds, alcohol-based compounds, phenol-based compounds, active methylene-based compounds, amine-based compounds, imine-based compounds, oxime-based compounds, carbamic acid-based compounds, urea-based compounds, acid amide-based (lactam-based) compounds, acid imide-based compounds, triazole-based compounds, pyrazole-based compounds, mercaptan-based compounds, bisulfites, and the like.

[0081] Examples of the imidazole-based compounds, for example, imidazole (Dissociation temperature of 100°C), benzimidazole (Dissociation temperature of 120°C), 2-methylimidazole (Dissociation temperature of 70°C), 4-methylimidazole (Dissociation temperature of 100°C), 2-ethylimidazole (Dissociation temperature of 70°C), 2-isopropylimidazole, 2,4-dimethylimidazole, 2-ethyl-4-methylimidazole, and the like.

[0082] Examples of the imidazoline-based compounds include 2-methylimidazoline (Dissociation temperature of 110°C), 2-phenylimidazoline, and the like, for example.

[0083] Examples of the pyrimidine-based compound include 2-methyl-1,4,5,6-tetrahydropyrimidine and the like, for example.

[0084] Examples of the guanidine-based compounds include, for example, 3,3-dialkyl guanidine, such as 3,3-dimethyl guanidine, e.g., 1,1,3,3-tetraalkyl guanidine, such as 1,1,3,3-tetramethyl guanidine (Dissociation temperature of 120°C), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, and the like.

[0085] Examples of the alcohol-based compounds include, for example, methanol, ethanol, 2-propanol, n-butanol, s-butanol, 2-ethylhexyl alcohol, 1- or 2-octanol, cyclohexyl alcohol, ethylene glycol, benzyl alcohol, 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol, 2-(hydroxymethyl)furan, 2-methoxyethanol, methoxy propanol, 2-ethoxyethanol, n-propoxyethanol, 2-butoxyethanol, 2-ethoxyethoxyethanol, 2-ethoxybutoxyethanol, butoxyethoxyethanol, 2-butoxyethylethanol, 2-butoxyethoxyethanol, N,N-dibutyl-2-hydroxyacetamide, N-hydroxysuccinimide, N-morpholine ethanol, 2,2-dimethyl-1,3-dioxolane-4-methanol, 3-oxazolidine ethanol, 2-hydroxymethyl pyridine (Dissociation temperature of 140°C), furfuryl alcohol, 12-hydroxy stearic acid, triphenyl silanol, 2-hydroxyethyl methacrylate, and the like.

[0086] Examples of the phenol-based compounds include, for example, phenol, cresol, ethylphenol, n-propylphenol, isopropylphenol, n-butylphenol, s-butylphenol, t-butylphenol, n-hexylphenol, 2-ethylhexylphenol, n-octylphenol, n-nonylphenol, di-n-propylphenol, diisopropylphenol, isopropylcresol, di-n-butylphenol, di-s-butylphenol, di-t-butylphenol, di-n-octylphenol, di-2-ethylhexylphenol, di-n-nonylphenol, nitrophenol, bromophenol, chlorophenol, fluorophenol, dimethylphenol, styrenated phenol, methylsalicylate, 4-hydroxymethylbenzoate, 4-hydroxybenzylbenzoate, 2-ethylhexyl hydroxybenzoate, 4-[(dimethylamino)methyl]phenol, 4-[(dimethylamino)methyl]nonylphenol, bis(4-hydroxyphenyl)acetate, 2-hydroxypyridine (Dissociation temperature of 80°C), 2- or 8-hydroxyquinoline, 2-chloro-3-pyridinol, pyridine-2-thiol (Dissociation temperature of 70°C), and the like.

[0087] Examples of the active methylene-based compounds include, for example, Meldrum's acid, dialkyl malonates (e.g., dimethyl malonate, diethyl malonate, di n-butyl malonate, di-t-butyl malonate, di 2-ethylhexyl malonate, methyl n-butyl malonate, ethyl n-butyl malonate, methyl s-butyl malonate, ethyl s-butyl malonate, methyl t-butyl malonate, ethyl t-butyl malonate, diethyl methylmalonate, dibenzyl malonate, diphenyl malonate, benzylmethyl malonate, ethylphenyl malonate, t-butylphenyl malonate, isopropylidene malonate, and the like), alkyl acetoacetates (e.g., methyl acetoacetate, ethyl acetoacetate, n-propyl acetoacetate, isopropyl acetoacetate, n-butyl acetoacetate, t-butyl acetoacetate, benzyl acetoacetate, phenyl acetoacetate, and the like), 2-acetoacetoxyethyl methacrylate, acetylacetone, ethyl cyanoacetate, and the like.

[0088] Examples of the amine compounds include, for example, dibutylamine, diphenylamine, aniline, N-methylaniline, carbazole, bis(2,2,6,6-tetramethylpiperidiny)amine, di-n-propylamine, diisopropylamine (Dissociation temperature of 130°C), isopropylethylamine, 2,2,4- or 2,2,5-trimethylhexamethylenamine, N-isopropylcyclohexylamine (Dissociation temperature of 140°C), dicyclohexylamine (Dissociation temperature of 130°C.), bis(3,5,5-trimethylcyclohexyl)amine, piperidine, 2,6-dimethylpiperidine (Dissociation temperature of 130°C), t-butylmethylamine, t-butylethylamine (Dissociation temperature 120°C), t-butylpropylamine, t-butylbutylamine, t-butylbenzylamine (Dissociation temperature of 120°C), t-butylphenylamine, 2,2,6-trimethylpiperidine, 2,2,6,6-tetramethylpiperidine (Dissociation temperature of 80°C), (dimethylamino)-2,2,6,6-tetramethylpiperidine, 2,2,6,6-tetramethyl-4-piperidine, 6-methyl-2-piperidine, 6-aminocaproic acid, and the like.

[0089] Examples of the imine compounds include, for example, ethyleneimine, polyethyleneimine, 1,4,5,6-tetrahydropyrimidine, guanidine, and the like.

[0090] Examples of the oxime compounds include, for example, formaldoxime, acetaldoxime, acetoxime, methylethylketoxime (Dissociation temperature of 130°C), cyclohexanoneoxime, diacetyl monoxime, benzophenone oxime, 2,2,6,6-tetramethylcyclohexanoneoxime, diisopropylketoneoxime, methyl t-butylketoneoxime, diisobutylketoneoxime, methylisobutylketoneoxime, methylisopropylketoneoxime, methyl 2,4-dimethylpentylketoneoxime, methyl 3-ethylheptylketoneoxime, methylisoamylketoneoxime, n-amylketoneoxime, 2,2,4,4-tetramethyl-1,3-cyclobutanedionemonooxime, 4,4'-dimethoxybenzophenoneoxime, 2-heptanoneoxime, and the like.

[0091] Examples of the carbamic acid compounds include, for example, phenyl N-phenyl carbamate and the like.

[0092] Examples of the urea compounds include, for example, urea, thiourea, ethylene urea, and the like.

[0093] Examples of the acid amide-based (lactam-based) compounds include, acetanilide, N-methyl acetamide, acetamide, ϵ -caprolactam, δ -valerolactam, γ -butyrolactam, pyrrolidone, 2,5-piperazine dione, laurilactam, and the like, for example.

[0094] Examples of the acid imide compounds include succinimide, maleinimide, phthalimide, and the like, for example.

[0095] Examples of the triazole compounds include 1,2,4-triazole, benzotriazole, and the like, for example.

[0096] Examples of the pyrazole compounds include pyrazole, 3,5-dimethylpyrazole (Dissociation temperature of 120°C), 3,5-diisopropylpyrazole, 3,5-diphenylpyrazole, 3,5-di-*t*-butylpyrazole, 3-methylpyrazole, 4-benzyl-3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, 4-bromo-3,5-dimethylpyrazole, 3-methyl-5-phenylpyrazole, and the like, for example.

[0097] Examples of the mercaptan compounds include butylmercaptan, dodecylmercaptan, hexylmercaptan, and the like, for example.

[0098] Examples of the bisulfates include sodium bisulfate and the like, for example.

[0099] Examples of the blocking agent also include, for example, other blocking agents, such as benzoxazolone, isatoic acid anhydride, and tetrabutylphosphonium acetate, without being limited to the above-described examples.

[0100] For some of the compounds illustrated above, the dissociation temperature is also indicated. This is the temperature for regenerating the isocyanate group.

[0101] Such blocking agents can be used alone or in combination of two or more kinds thereof. The dissociation temperature of the blocking agent can be selected as appropriate. The dissociation temperature is 60°C or more and 230°C or less, preferably 80°C or more and 200°C or less, more preferably 100°C or more and 180°C or less, and still more preferably 110°C or more and 160°C or less, for example. Within such a temperature range, the pot life of the pigment textile printing ink jet ink composition can be sufficiently lengthened and the temperature in a heating process can be prevented from being excessively high.

[0102] The main chain of the urethane-based resin having a crosslinkable group may be any one of a polyether type containing an ether bond, a polyester type containing an ester bond, and a polycarbonate type containing a carbonate bond. The elongation at fracture point and the 100% modulus when the urethane-based resin having a crosslinkable group is crosslinked (crosslinked object) can be adjusted by changing the density of the crosslinking point and the kind of such a main chain. Among the above examples, it is more preferable to use a urethane-based resin having a crosslinkable group and a polycarbonate-based or polyether-based skeleton in order to ensure that the balance between the elongation at fracture point and the 100% modulus is good such the rubbing fastness of an image and the texture of a printed textile are improved. A polycarbonate-based urethane resin having a polycarbonate-based skeleton is particularly preferable because the polycarbonate-based urethane resin tends to be able to improve the rubbing fastness. In particular, because the pigment textile printing ink jet ink composition to be used in the invention contains a nonionic fluorine-based surfactant, there is a tendency that the rubbing fastness of a printed textile to be obtained is likely to be poor. However, by the use of polycarbonate-based urethane resin particles as the resin particles, the pigment is likely to be fixed to the surface of a fabric and, even when a nonionic fluorine-based surfactant is used, a printed textile with excellent color developability and rubbing fastness is obtained.

[0103] The urethane-based resin having a crosslinkable group has an elongation at fracture point after crosslinking (crosslinked object) of 150% or more, preferably 170% or more, more preferably 200% or more, and still more preferably 300% or more. By selecting the density of the crosslinking point and the kind of the main chain so as to have such an elongation at fracture point, the texture of a printed textile can be improved.

[0104] Herein, the elongation at fracture point and the 100% modulus are obtained by carrying out measurements on a film obtained by curing a urethane-based resin emulsion having a crosslinkable group to create a film having a thickness of about 60 μ m. Elongation at fracture point is measured under the conditions of the tensile test gauge length of 20 mm and the tensile speed of 100 mm/min. The 100% modulus is a value obtained by measuring the tensile stress when the film is 100% elongated relative to the original length in the tensile test. The film to be measured may be formed using a urethane-based resin emulsion having a crosslinkable group or may be formed by molding a urethane resin. Formation using an emulsion resin is preferable.

[0105] The urethane-based resin having a crosslinkable group may be provided in the form of an emulsion. Such a resin emulsion is a so-called self-reaction type urethane-based resin emulsion and suitable commercially available emulsions include urethane-based resin emulsions having an isocyanate group blocked by a blocking agent having a hydrophilic group.

[0106] Examples commercially-available urethane-based resins having a crosslinkable group include TAKELAC WS-6021 (Trade Name, manufactured by Mitsui Chemicals Polyurethanes Inc., urethane-based resin emulsion, polyether-based polyurethane having a polyether-derived skeleton), WS-5100 (Trade Name, manufactured by Mitsui Chemicals Polyurethanes Inc., urethane-based resin emulsion, polycarbonate-based polyurethane having a polycarbonate-derived skeleton), Elastron E-37 and H-3 (polyester-based polyurethane, the main chain of which has a polyester-derived skel-

eton), Elastron H-38, BAP, C-52, F-29, and W-11P (polyether-based polyurethane, the main chain of which has a polyether-derived skeleton) (Trade Names, manufactured by Daiichi Kogyo Seiyaku Co., Ltd. urethane-based resin emulsion), SUPERFLEX 870, 800, 150, 420, 460, 470, 610, and 700 (Trade Names, manufactured by Daiichi Kogyo Seiyaku Co., Ltd., urethane-based resin emulsion), PARMARIN UA-150 (Trade Name, manufactured by Sanyo Chemical Industries, Ltd., urethane-based resin emulsion), Sancure 2710 (Trade Name, manufactured by Japan Lubrizol Corporation., urethane-based resin emulsion), NeoRez R-9660, R-9637, and R-940 (Trade Names, manufactured by Kusumoto Chemicals, Ltd., urethane-based resin emulsion), ADEKABON TITER HUX-380 and 290K (Trade Names, manufactured by ADEKA, Inc., urethane-based resin emulsion) and the like.

[0107] In the invention, the content of the resin particles is preferably 1% by mass or more and 20% by mass or less in terms of solid content based on the total mass (100% by mass) of the ink and the lower limit is more preferably 2.5% by mass or more and still more preferably 3% by mass or more. The upper limit of the content of the resin particles is more preferably 15% by mass or less and still more preferably 12% by mass or less. By setting the content of the resin particles within the range mentioned above, suitable values for both the discharge stability and the rubbing fastness of a recorded material can be achieved.

[0108] A treatment liquid according to the invention may also comprise a urethane-based resin. In that case, the urethane-based resin contained in the treatment liquid may be the same as or different from the urethane-based resin contained in the pigment textile printing ink jet ink composition.

[0109] The temperature in a heating process in the ink jet pigment textile printing method according to the invention described below is set considering the deprotection temperature (dissociation temperature) of the isocyanate group of the urethane-based resins having a crosslinkable groups so that at least some of the crosslinkable groups are activated.

2.3. Surfactant

[0110] The pigment textile printing ink jet ink composition to be used in the invention may contain surfactants. The surfactants have functions of reducing the surface tension of an ink composition, increasing the wettability with a fabric, and the like, and thus facilitates the achievement of a desired viscosity and surface tension of an ink required in the ink jet pigment textile printing method according to the invention.

[0111] Suitable surfactants include acetylene glycol-based surfactants, acetylene alcohol-based surfactants, silicone-based surfactants, and fluorine-based surfactants. In particular, it is preferable to use silicone-based surfactants and fluorine-based surfactants since these allow the surface tension of an ink composition to be easily adjusted to a desired value.

[0112] Examples of acetylene glycol-based surfactants include, but are not particularly limited to, Surfynol 104, 104E, 104H, 104A, 104BC, 104DPM, 104PA, 104PG-50, 104S, 420, 440, 465, 485, SE, SE-F, 504, 61, DF37, CT111, CT121, CT131, CT136, TG, GA, and DF110D (all Trade Names, manufactured by Air Products and Chemicals, Inc.), Olefin B, Y, P, A, STG, SPC, E1004, E1010, PD-001, PD-002W, PD-003, PD-004, EXP.4001, EXP.4036, EXP.4051, AF-103, AF-104, AK-02, SK-14, and AE-3 (all Trade Names, manufactured by Nisshin Chemical Co., Ltd.), and Acetylenol E00, E00P, E40, and E100 (all Trade Names, manufactured by Kawaken Fine Chemicals Co., Ltd. make).

[0113] The silicone-based surfactants are not particularly limited, although polysiloxane-based compounds are preferred. The polysiloxane-based compounds are not particularly limited and include, for example, polyether-modified organosiloxanes. Examples of commercially-available polyether-modified organosiloxanes include: BYK-306, BYK-307, BYK-333, BYK-341, BYK-345, BYK-346, and BYK-348 (all Trade Names, manufactured by BYK Chemie Japan, Inc.), KF-351A, KF-352A, KF-353, KF-354L, KF-355A, KF-615A, KF-945, KF-640, KF-642, KF-643, KF-6020, X-22-4515, KF-6011, KF-6012, KF-6015, and KF-6017 (all Trade Names, manufactured by Shin-Etsu Chemical Co., Ltd.).

[0114] As the fluorine-based surfactants, fluorine-modified polymers are preferably used and BYK-340 (BYK Chemie Japan, Inc.) is mentioned as a specific example.

[0115] The lower limit of the content of the surfactant is preferably 0.1% by mass or more, more preferably 0.3% by mass or more, and still more preferably 0.5% by mass or more based on the total mass (100% by mass) of the ink. The upper limit of the content of the surfactant is preferably 10% by mass or less, more preferably 7% by mass or less, still more preferably 5% by mass or less, particularly preferably 2% by mass or less, and yet still more preferably 1% by mass or less based on the total mass (100% by mass) of the ink.

[0116] In the invention, the fluorine-based surfactants are preferably nonionic fluorine-based surfactants. When a nonionic fluorine-based surfactant is used, permeation of the ink into the fabric is suppressed. The nonionic fluorine-based surfactant holds the ink on the surface of the fabric and thus the sinking of the pigment into the fabric is suppressed. Due to the fact that the surfactant is nonionic, unevenness in color development hardly occurs. Therefore, because the pigment textile printing ink jet ink composition to be used in the invention contains a nonionic fluorine-based surfactant, a printed textile having excellent color developability can be obtained.

[0117] When the pigment textile printing ink jet ink composition to be used in the invention is used for two-layer printing, blurring of a color boundary with a chromatic color ink (hereinafter also referred to as "color ink") to be printed later can be decreased by reducing the wettability of the surface of a white base formed of a white ink containing a white pigment as the pigment of the pigment textile printing ink jet ink composition, and therefore the color developability of the chromatic

color ink is improved.

[0118] When selecting the nonionic fluorine-based surfactant, it is preferable to take the HLB value into consideration. More specifically, the lower limit of the HLB value of the nonionic fluorine-based surfactant compounded in the pigment textile printing ink jet ink composition is 6 or more, preferably 8 or more, and more preferably 10 or more. The upper limit of the HLB value of the nonionic fluorine-based surfactant is 15 or less, preferably 13 or less, and more preferably 12 or less. The nonionic fluorine-based surfactant having an HLB value within the range mentioned above has higher hydrophilicity and more easily suppresses the permeability into a fabric of the pigment textile printing ink jet ink composition. Therefore, the color developability can be further improved.

[0119] The HLB value in this specification is a value calculated by the following expression (1) from the ratio of a nonpolar value (I) and a polar value (O) in an organic conceptual diagram (hereinafter also simply referred to as "I/O value").

$$HLB\ value = \left(\frac{Nonpolar\ value\ (I)}{Polar\ value\ (O)} \right) \times 10 \quad (1)$$

[0120] Specifically, the I/O value can be calculated based on each of the literatures of "Keitoteki Yuki Teisei Bunseki Kongobutsu Hen" (Systematic Organic Qualitative Analysis (Mixtures)), edited by Atsushi FUJITA, Kazama shobo, 1974; "Senshoku Riron Kagaku" (Dyeing Theory Science), edited by Nobuhiko KUROKI, Maki Shoten, 1966; and "Yuki Kagobutshu Bunriho" (Organic compound Separation Method), edited by Hiroo INOUE, Shokabo, 1990.

[0121] The nonionic fluorine-based surfactant preferably has a polyoxyethylene group and an alkyl fluoride group, and a polyfluoroalkylamine oxide or a polyfluoroalkyl-alkylene oxide adduct is preferable.

[0122] As the nonionic fluorine-based surfactant to be used in the invention, commercially available substances are usable and examples include Surflon S-145, Surflon S-241, Surflon S-242, Surflon S-243, Surflon S-386, Surflon S-393, Surflon S-420, Surflon S-611, Surflon S-650, Surflon S-651, Surflon KH-20, and Surflon KH-40 (all Trade Names, manufactured by AGC SEIMI CHEMICAL CO., LTD.), Fluorad FC-170C, Fluorad FC-430, and Fluorad FC4430 (all Trade Names, manufactured by Sumitomo 3M Japan, Inc.), FSO, FSO-100, FSN, FSN-100, and FS-300 (all Trade Names, manufactured by DuPont), Ftergent FT-250 and 251 (all Trade Names, manufactured by Neos Co., Ltd.), Megafac F-554 and Megafac F-556 (all Trade Names, manufactured by DIC, Inc.), and the like. Among the above, FSO, FSO-100, FSN, FSN-100, and FS-300 of DuPont are preferably used. By the use of the nonionic fluorine-based surfactants, the permeability into a fabric of the pigment textile printing ink jet ink composition can be controlled, so that the color developability of a printed textile can be further improved. When the pigment textile printing ink jet ink composition to be used in the invention is used for two-layer printing, the blurring of a color boundary with a chromatic color ink printed later can be decreased by reducing the wettability of the surface of a white base formed of a white ink, so that the color developability of the chromatic color ink is improved.

[0123] The lower limit of the content of the nonionic fluorine-based surfactant of the pigment textile printing ink jet ink composition to be used in the invention is preferably 0.1% by mass or more, more preferably 0.2% by mass or more, and still more preferably 0.3% by mass or more based on the total mass (100% by mass) of the pigment textile printing ink jet ink composition. The upper limit of the content of the nonionic fluorine-based surfactant is preferably 0.8% by mass or less, more preferably 0.6% by mass or less, and still more preferably 0.5% by mass or less based on the total mass (100% by mass) of the pigment textile printing ink jet ink composition. When the content of the nonionic fluorine-based surfactant is within the range mentioned above, the permeability into the fabric of the pigment textile printing ink jet ink composition can be controlled, so that the color developability of a printed textile can be further improved. When the pigment textile printing ink jet ink composition to be used in the invention is used for the two-layer printing, the blurring of a color boundary with a chromatic color ink printed later can be decreased by reducing the wettability of the surface of a white base formed of a white ink, so that the color developability of the chromatic color ink is improved.

[0124] When the pigment textile printing ink jet ink composition set to be used in the invention is used for two-layer printing, the content of the nonionic fluorine-based surfactant in the chromatic color pigment textile printing ink jet ink composition is preferably 0.5% by mass or less, more preferably 0.3% by mass or less, and still more preferably 0.1% by mass or less based on the total mass (100% by mass) of the chromatic color pigment textile printing ink jet ink composition. In some cases, the chromatic color pigment textile printing ink jet ink composition does not contain a nonionic fluorine-based surfactant. Due to the fact that the content of the nonionic fluorine-based surfactant in the chromatic color pigment textile printing ink jet ink composition is low, a reduction in rubbing fastness of a printed textile is suppressed in two-layer printing, so that an image with good abrasion resistance is obtained.

2.4. Water

[0125] The pigment textile printing ink jet ink composition to be used in the invention contains water as a solvent. The

water is a medium serving as the main component of the ink and is a component which is evaporated and scattered by drying. Suitably, the water contains as few ionic impurities as possible, and examples of suitable water types include pure water and ultrapure water, e.g., ion exchanged water, ultrafiltration water, reverse osmosis water, and distilled water. When water sterilized by irradiation with ultraviolet rays or the addition of hydrogen peroxide, for example, is used, the generation of molds or bacteria can be prevented when the ink is stored over a long period of time.

[0126] The content of the water contained in the pigment textile printing ink jet ink composition to be used in the invention is not particularly limited and can be 50% by mass or more, can be 60% by mass or more, or can be 70% by mass or more based on the total mass (100% by mass) of the ink. The upper limit of the content of the water contained in the ink can be 95% by mass or less, can be 90% by mass or less, and can be 80% by mass or less.

2.5. Water-soluble organic solvent

[0127] The pigment textile printing ink jet ink composition to be used in the invention may also contain a water-soluble organic solvent. Due to the presence of the water-soluble organic solvent, the discharge stability by an ink jet method of the ink composition is improved and moisture evaporation from an ink jet head when allowed to stand over a long period of time can be effectively suppressed.

[0128] Examples of the water-soluble organic solvent include polyol compounds, glycol ethers, betaine compounds, and the like.

[0129] The polyol compounds may be polyol compounds (preferably diol compounds) in which the number of carbon atoms in the molecules is 2 or more and 6 or less and which may have one ether bond in the molecules. Specific examples of the polyol compounds include glycols, such as 1,2-pentanediol, methyl triglycol (triethylene glycol monomethyl ether), butyl triglycol (triethylene glycol monobutyl ether), butyl diglycol (diethylene glycol monobutyl ether), dipropylene glycol monopropyl ether, glycerol, 1,2-hexanediol, 1,2-heptanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 2-methyl-3-phenoxy-1,2-propanediol, 3-(3-methylphenoxy)-1,2-propanediol, 3-hexyloxy-1,2-propanediol, 2-hydroxymethyl-2-phenoxy methyl-1,3-propanediol, 3-methyl-1,3-butanediol, 1,3-propanediol, 1,2-butanediol, 1,2-pentanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-2,4-pentanediol, and 3-methyl-1,5-pentanediol.

[0130] Suitable glycol ethers include monoalkyl ethers of glycols selected from ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycols, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, and polyoxyethylene polyoxy propylene glycol are preferable, for example. More preferably, triethylene glycol monomethyl ether, triethylene glycol monobutyl ether, dipropylene glycol monopropyl ether, and the like.

[0131] The betaine compounds are compounds (intramolecular salts) which have positive charges and negative charges at positions which are not adjacent to each other in the same molecule, in which a hydrogen atom which can be dissociated is not bonded to an atom having a positive charge, and which have no charges as whole molecules. The betaine compounds are preferably N-alkyl substitution products of amino acids and more preferably N-trialkyl substitution products of amino acids. Suitable betaine compounds include trimethyl glycine (also referred to as "glycine betaine"), γ -butyrol betaine, homarine, trigonelline, carnitine, homoserine betaine, valine betaine, lysine betaine, ornithine betaine, alanine betaine, stachydrine, glutamic acid betaine, and the like, and trimethyl glycine is preferred.

[0132] As the water-soluble organic solvent, pyrrolidone derivatives may be used. Examples of the pyrrolidone derivatives include N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 2-pyrrolidone, N-butyl-2-pyrrolidone, 5-methyl-2-pyrrolidone, and the like.

[0133] A single water-soluble organic solvent or a mixture of two or more such solvents may be used. The water-soluble organic solvent is preferably added so as to achieve a desired ink viscosity and surface tension as described below. The content of the water-soluble organic solvent is 0.2% by mass or more and 30% by mass or less, preferably 0.4% by mass or more and 20% by mass or less, more preferably 0.5% by mass or more and 15% by mass or less, and still more preferably 0.7% by mass or more and 10% by mass or less based on the total mass (100% by mass) of the ink.

2.6. Inorganic alkaline compound

[0134] The pigment textile printing ink jet ink composition to be used in the invention preferably contains an inorganic alkaline compound (inorganic base compound). The inorganic alkaline compound has a property of increasing the pH of the pigment textile printing ink jet ink composition. The inorganic alkaline compound has the function of increasing the dispersion stability of resin particles and/or improving the redispersibility of resin particles.

[0135] Examples of the inorganic alkaline compound include hydroxides of alkali metals or hydroxides of alkaline earth metals, carbonates of alkali metals or carbonates of alkaline earth metals, phosphates of alkali metals or phosphates of alkaline earth metals, and the like.

[0136] Examples of the hydroxides of alkali metals include lithium hydroxide, sodium hydroxide, potassium hydroxide, and the like. Examples of the hydroxide of alkaline earth metals include calcium hydroxide, magnesium hydroxide, and

the like.

[0137] Examples of the carbonates of alkali metals include lithium carbonate, lithium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, sodium carbonate, sodium hydrogen carbonate, and the like. Examples of the carbonates of alkaline earth metals include calcium carbonate and the like.

[0138] Examples of the phosphates of alkali metals include lithium phosphate, potassium phosphate, potassium dihydrogen phosphate, trisodium phosphate, disodium hydrogen phosphate, and the like. Examples of the phosphates of alkaline earth metals include calcium phosphate, calcium hydrogen phosphate, and the like.

[0139] In the pigment textile printing ink jet ink composition to be used in the invention, a single inorganic alkaline compound mentioned above or a mixture of two or more of such compounds may be used. The total content of the inorganic alkaline compound is 0.01% by mass or more and 0.8% by mass or less, preferably 0.02% by mass or more and 0.6% by mass or less, more preferably 0.03% by mass or more and 0.4% by mass or less, still more preferably 0.04% by mass or more and 0.3% by mass or less, particularly preferably 0.05% by mass or more and 0.2% by mass or less, and more particularly preferably 0.05% by mass or more and 0.1% by mass or less based on the total mass (100% by mass) of the pigment textile printing ink jet ink composition.

[0140] When the amount of the inorganic alkaline compound is within the range mentioned above, the pH of the pigment textile printing ink jet ink composition can be sufficiently increased such that the dispersion stability of resin particles is increased and/or the redispersibility of resin particles is improved.

2.7. Other components

[0141] The pigment textile printing ink jet ink composition to be used in the invention may contain pH adjusters, antiseptic agents, antifungal agents, antirusts, chelating agents, viscosity modifiers, dissolution assistants, antioxidants, and the like as necessary. pH adjuster

[0142] Examples of the pH adjusters include morpholines, piperazines, amines having a normal boiling point at 25°C of 200°C or more, such as diethanolamine, triethanolamine, and triisopropanolamine, ammonia, and the like as well as the inorganic alkali compounds described above. Amines having a normal boiling point at 25°C of 200°C or more are preferred pH adjusters. When the inkjet ink composition contains such high boiling point amines, clogging of a head can be suppressed at the operating temperature of a heating process in the ink jet pigment textile printing method according to the invention and described below.

Antiseptic agent and antifungal agent

[0143] Examples of suitable antiseptic agents and antifungal agents include sodium benzoate, sodium pentachlorophenol, sodium 2-pyridinethiol-1-oxide, sodium sorbate, sodium dehydroacetate, 1,2-dibenzine thiazoline-3-one (Proxel CRL, Proxel BND, Proxel GXL, Proxel XL-2, and Proxel TN of ICI), and the like.

Chelating agent

[0144] The chelating agent has a property of capturing ions. Examples of suitable chelating agents include ethylenediaminetetraacetate (EDTA), nitrilotriacetate, hexametaphosphate, pyrophosphate, or metaphosphate of ethylene diamine, and the like.

2.8. Method for preparing pigment textile printing ink jet ink composition

[0145] The pigment textile printing ink jet ink composition to be used in the invention is obtained by mixing the components mentioned above in an arbitrary order, and then performing filtration or the like as necessary to remove impurities. Preferably, the method for mixing the components comprises successively adding materials into a container provided with a stirring device, such as a mechanical stirrer or a magnetic stirrer, and then stirring and mixing the components. Filtration methods such as centrifugal filtration, filter filtration, and the like can be performed as necessary.

2.9. Physical properties of pigment textile printing ink jet ink composition

[0146] The pigment textile printing ink jet ink composition to be used in the invention is applied to a fabric by an ink jet method. Therefore, in the pigment textile printing ink jet ink composition, the surface tension at 25°C is preferably 10 mN/m or more and 40 mN/m or less and more preferably 25 mN/m or more and 40 mN/m or less from the viewpoint of the balance between the recording quality and the reliability as an ink for ink jet recording. For the measurement of the surface tension, the measurement can be performed by confirming the surface tension when a platinum plate is wetted with an ink in a 25°C environment using an automatic surface tensiometer CBVP-Z (Trade Name, manufactured by

Kyowa Interface Science Co., LTD.), for example.

[0147] From the same viewpoint, the viscosity at 20°C of the pigment textile printing ink jet ink composition is preferably 2 mPa·s or more and 15 mPa·s or less, more preferably 2 mPa·s or more and 5 mPa·s or less, and more preferably 2 mPa·s or more and 3.6 mPa·s or less. The viscosity in a 40°C or 20°C environment can be measured using a viscoelasticity testing machine MCR-300 (Trade Name, manufactured by Pysica), for example.

3. Treatment liquid composition for ink jet pigment textile printing

[0148] Next, the treatment liquid composition for ink jet pigment textile printing according to the invention is described. The treatment liquid composition for ink jet pigment textile printing according to the invention is a treatment liquid composition which coagulates the components of the ink composition described above in ink jet pigment textile printing, which is used by being attached to a fabric, and which comprises a cationic compound, a nonionic fluorine-based surfactant, resin particles, and water. The treatment liquid preferably does not contain a colouring agent. Thus, it is preferred that the treatment liquid does not contain a pigment or a dye.

[0149] The treatment liquid composition for ink jet pigment textile printing according to the invention may be comprised in a treatment liquid composition set for ink jet pigment textile printing. The treatment liquid composition set for ink jet pigment textile printing according to the invention contains the treatment liquid composition for ink jet pigment textile printing according to the invention and the pigment textile printing ink jet ink composition described above.

3.1. Cationic compound

[0150] The treatment liquid composition for ink jet pigment textile printing according to the invention contains a cationic compound. The cationic compound acts as a coagulant coagulating the components of the ink composition described above. Examples of suitable cationic compounds include polyvalent metal salts, organic acids, cationic resins, cationic surfactants, and the like. The cationic compounds may be used alone or two or more such compounds may be used in combination. Preferred cationic compounds include polyvalent metal salts, organic acids and cationic resins and polyvalent metal salts are more preferred as these have excellent reactivity with the pigment and the resin particles contained in the ink composition.

[0151] The polyvalent metal salts are compounds containing polyvalent metal ions of divalent or more and anions bonded to the polyvalent metal ions and are soluble in water. Specific examples of the polyvalent metal ions include divalent metal ions, such as Ca^{2+} , Cu^{2+} , Ni^{2+} , Mg^{2+} , Zn^{2+} , and Ba^{2+} , and trivalent metal ions, such as Al^{3+} , Fe^{3+} , and Cr^{3+} . Examples of anions include Cl^- , I^- , Br^- , SO_4^{2-} , ClO_3^- , NO_3^- , HCOO^- , CH_3COO^- , and the like. Among such polyvalent metal salts, calcium salts and magnesium salts are preferable, particularly either calcium nitrate or calcium chloride as these enhance the stability of the treatment liquid and the reactivity as a coagulant.

[0152] Suitable organic acids include sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, polyacrylic acid, acetic acid, glycolic acid, malonic acid, malic acid, maleic acid, ascorbic acid, succinic acid, glutaric acid, fumaric acid, citric acid, tartaric acid, lactic acid, sulfonic acid, orthophosphoric acid, pyrrolidone carboxylic acid, pyrone carboxylic acid, pyrrole carboxylic acid, furancarboxylic acid, pyridinecarboxylic acid, coumaric acid, thiophene carboxylic acid, nicotinic acid, or derivatives of these compounds or salts thereof. The organic acids may be used alone or in combination of two or more kinds thereof.

[0153] Examples of the cationic resin include cationic urethane resins, cationic olefin resins, cationic allylamine resins, and the like.

[0154] As the cationic urethane resin, known substances can be selected and used as appropriate. As the cationic urethane resin, commercially-available items are usable and, for example, HYDRAN CP-7010, CP-7020, CP-7030, CP-7040, CP-7050, CP-7060, and CP-7610 (Trade Names, manufactured by Dainippon Ink and Chemicals, Incorporated), SUPERFLEX 600, 610, 620, 630, 640, and 650 (Trade Names, manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), urethane emulsions WBR-2120C and WBR-2122C (Trade Names, manufactured by TAISEI FINE CHEMICAL CO., LTD.), and the like are usable.

[0155] The cationic olefin resin has olefins, such as ethylene and propylene, in the structure skeleton and known substances can be selected and used as appropriate. The cationic olefin resin may be in an emulsion state and be dispersed in a solvent containing water or an organic solvent. As the cationic olefin resin, commercially-available items are usable and examples include Arrow Base CB-1200 and CD-1200 (Trade Names, manufactured by a UNITIKA LTD.) and the like.

[0156] As the cationic allylamine resin, known substances can be selected and used as appropriate. Examples include polyallylamine hydrochloride, polyallylamine amide sulfate, an allylamine hydrochloride-diallylamine hydrochloride copolymer, an allylamine acetate-diallylamine acetate copolymer, an allylamine acetate-diallylamine acetate copolymer, an allylamine hydrochloride-dimethyl allylamine hydrochloride copolymer, an allylamine-dimethyl allylamine copolymer, polydiallylamine hydrochloride, polymethyl diallylamine hydrochloride, polymethyl diallylamine amide sulfate, polymethyl

diallylamine acetate, polydiallyl dimethyl ammonium chloride, a diallylamine acetate-sulfur dioxide copolymer, a diallyl methyl ethylammonium ethylsulfate-sulfur dioxide copolymer, a methyl diallylamine hydrochloride-sulfur dioxide copolymer, a diallyl dimethyl ammonium chloride-sulfur dioxide copolymer, a diallyl dimethyl ammonium chloride-acryl amide copolymer, and the like. As such a cationic allylamine-based resin, commercially available items are usable, for example,

PAA-HCL-01, PAA-HCL-03, PAA-HCL-05, PAA-HCL-3L, PAA-HCL-10L, PAA-H-HCL, PAA-SA, PAA-01, PAA-03, PAA-05, PAA-08, PAA-15, PAA-15C, PAA-25, PAA-H-10C, PAA-D11-HCL, PAA-D41-HCL, PAA-D19-HCL, PAS-21CL, PAS-M-1L, PAS-M-1, PAS-22SA, PAS-M-1A, PAS-H-1L, PAS-H-5L, PAS-H-10L, PAS-92, PAS-92A, PAS-J-81L, and PAS-J-81 (Trade Names, manufactured by NITTOBO MEDICAL CO., LTD.), Himo Neo-600, Himoloc Q-101, Q-311, and Q-501, Himax SC-505 and SC-505 (Trade Names, manufactured by HYMO Co., Ltd.), and the like.

[0157] As the cationic resin, compounds obtained by polymerizing monomers containing amine and epihalohydrin compounds may also be used. Such compounds have increased buffering action and, when contacting an ink, they are able to coagulate pigments due to the fact that they contain hydroxyl groups, ammonium cations, and the like in the main chain and can sequester halide anions from an aqueous solution. Examples of compounds obtained by polymerizing monomers containing amine and epihalohydrin include compounds selected from polyamine-epihalohydrin copolymers, polyamide-epihalohydrin copolymers or polyamide polyamine-epihalohydrin copolymers, and amine-epihalohydrin copolymers. The compounds are obtained by known methods, such as polymerizing monomers containing amine and epihalohydrin and graft-polymerizing monomers containing epihalohydrin with polyamide obtained by polymerizing monomers containing amine and carboxylic acid. The mass average molecular weight varies depending on the type of the copolymer. In the case of the polyamine epihalohydrin copolymer, the mass average molecular weight is preferably within the range of 500 to 100000, in the case of the polyamide-epihalohydrin copolymer or the polyamide polyamine-epihalohydrin copolymer, the mass average molecular weight is preferably within the range of 10000 to 5000000, and, in the case of the amine-epihalohydrin copolymer, the mass average molecular weight is preferably within the range of 700 to 50000. When the mass average molecular weight exceeds the upper limits mentioned above, the polymer may not be soluble in an aqueous solvent. When the lower limits are not satisfied, the pretreatment effect may decrease. Examples of suitable commercially-available polymers include WS-4020 (manufactured SEIKO PMC CORPORATION, polyamide-epichlorohydrin copolymer) and the like.

[0158] Examples of the cationic surfactants include primary, secondary, and tertiary amine salt-type compounds, alkylamine salts, dialkylamine salts, aliphatic amine salts, benzalkonium salts, quaternary ammonium salts, quaternary alkylammonium salts, alkyl pyridinium salts, sulfonium salts, phosphonium salts, onium salts, imidazolium salts, and the like. Specific examples of cationic surfactants include hydrochlorides, acetates, and the like of laurylamine, palm amine, rosin amine, and the like, lauryl trimethyl ammonium chloride, cetyl trimethyl ammonium chloride, benzyl tributyl ammonium chloride, benzalkonium chloride, dimethyl ethyl lauryl ammonium ethyl sulfate, dimethyl ethyl octyl ammonium ethyl sulfate, trimethyl lauryl ammonium hydrochloride, cetyl pyridinium chloride, cetyl pyridinium bromide, dihydroxyethyl lauryl amine, decyl dimethyl benzyl ammonium chloride, dodecyl dimethyl benzyl ammonium chloride, tetradecyl dimethyl ammonium chloride, hexadecyl dimethyl ammonium chloride, octadecyl dimethyl ammonium chloride, and the like.

[0159] The content of the cationic compound may be 0.1% by mass or more and 25% by mass or less, may be 0.2% by mass or more and 20% by mass or less, and may be 0.3% by mass or more and 10% by mass or less based on the total mass (100% by mass) of the treatment liquid, for example. The concentration of the coagulant may be 0.03 mol/kg or more in 1 kg of the treatment liquid. The concentration of the coagulant may be 0.1 mol/kg or more and 1.5 mol/kg or less and may be 0.2 mol/kg or more and 0.9 mol/kg or less in 1 kg of the treatment liquid.

3.2. Water

[0160] The treatment liquid composition for ink jet pigment textile printing according to the invention preferably contains water as the main solvent. The water is a component evaporating and scattering by drying after the treatment liquid is attached to a recording medium. Suitably, the water is as described above for the ink and therefore the illustration thereof is omitted. The content of the water contained in the treatment liquid can be set to 50% by mass or more, preferably 60% by mass or more, more preferably 70% by mass or more, and still more preferably 80% by mass or more, for example, based on the total mass (100% by mass) of the treatment liquid.

3.3. Nonionic fluorine-based surfactant

[0161] The treatment liquid composition for ink jet pigment textile printing according to the invention comprises a nonionic fluorine-based surfactant. In a pigment textile printing method using the treatment liquid composition for ink jet pigment textile printing according to the invention, the permeation of the ink into the fabric is suppressed, and thus the sinking of the pigment into the fabric is suppressed because the nonionic fluorine-based surfactant holds the ink on the surface of the fabric. Due to the fact that the surfactant is nonionic, unevenness in color development hardly occurs. Therefore, due to the fact that the treatment liquid composition for ink jet pigment textile printing according to the invention

contains the nonionic fluorine-based surfactant, a printed textile with excellent color developability can be obtained.

[0162] When the treatment liquid composition for ink jet pigment textile printing according to the invention is used for the two-layer printing, blurring of a color boundary with a chromatic color ink (hereinafter also referred to as "color ink") to be printed later can be decreased by reducing the wettability of the surface of a white base formed of a white ink containing a white pigment as the pigment of the pigment textile printing ink jet ink composition, and therefore the color developability of the chromatic color ink is improved.

[0163] When selecting the nonionic fluorine-based surfactant, it is preferable to take the HLB value into consideration. More specifically, the lower limit of the HLB value of the nonionic fluorine-based surfactant compounded in the treatment liquid composition for ink jet pigment textile printing is 6 or more, preferably 8 or more, and more preferably 10 or more. The upper limit of the HLB value of the nonionic fluorine-based surfactant is 15 or less, preferably 13 or less, and more preferably 12 or less. The nonionic fluorine-based surfactant having an HLB value within the range mentioned above has a higher hydrophilicity and more easily suppresses the permeability into a fabric of the pigment textile printing ink jet ink composition. Therefore, the color developability can be further improved.

[0164] The nonionic fluorine-based surfactant preferably has a polyoxyethylene group and an alkyl fluoride group, and a polyfluoroalkylamine oxide or a polyfluoroalkyl-alkylene oxide adduct is preferable.

[0165] As the nonionic fluorine-based surfactant to be used in the invention, the same substances as those of the pigment textile printing ink jet ink composition described above are usable.

[0166] The lower limit of the content of the nonionic fluorine-based surfactant of the treatment liquid composition for ink jet pigment textile printing according to the invention is preferably 0.1% by mass or more, more preferably 0.2% by mass or more, and still more preferably 0.3% by mass or more based on the total mass (100% by mass) of the treatment liquid composition for ink jet pigment textile printing. The upper limit of the content of the nonionic fluorine-based surfactant is preferably 0.8% by mass or less, more preferably 0.6% by mass or less, and still more preferably 0.5% by mass or less based on the total mass (100% by mass) of the treatment liquid composition for ink jet pigment textile printing.

3.4. Water-soluble organic solvent

[0167] To the treatment liquid composition for ink jet pigment textile printing according to the invention, a water-soluble organic solvent may be added. By adding the water-soluble organic solvent, the wettability of the treatment liquid to a recording medium can be improved. As the water-soluble organic solvent, the same organic solvents illustrated in the ink composition are usable. The content of the water-soluble organic solvent is not particularly limited and can be set to 1% by mass or more and 40% by mass or less, for example, based on the total mass (100% by mass) of the treatment liquid.

3.5. Resin particles

[0168] Resin particles (resin emulsion) may also be included in the treatment liquid composition for ink jet pigment textile printing according to the invention for the purpose of improving the rubbing fastness and suppressing fluffing of a fabric. The color developability is also improved by inclusion of the resin particles. As such resin particles, commercially-available items are usable. For example, in the case of a urethane resin, SUPERFLEX 500, 6E-2000, E-2500, E-4000, and R-5000 (Trade Names, manufactured by Daiichi Kogyo Seiyaku Co., Ltd.) and ADEKABON TITER HUX-822 and 830 (Trade Names, manufactured by ADEKA, Inc.) are mentioned. Examples of the vinyl acetate resin include Vinyblan 1245L, 2680, 2682, and 2684 (Trade Names, manufactured by Nisshin Chemical Co., Ltd.). Examples of the acrylic resin include, for example, VONCOAT AN-402, R-3310, and R-3360 (Trade Names, manufactured by Dainippon Ink, Inc.).

[0169] The lower limit of the content of the resin particles in the treatment liquid is preferably 1% by mass or more, more preferably 3% by mass or more, and still more preferably 5% by mass or more based on the total mass (100% by mass) of the treatment liquid composition for the ink jet pigment textile printing. The upper limit of the content of the resin particles is preferably 12% by mass or less, more preferably 10% by mass or less, and still more preferably 8% by mass or less based on the total mass (100% by mass) of the treatment liquid composition for the ink jet pigment textile printing. When the content of the resin particles in the treatment liquid is within the range mentioned above, the rubbing fastness can be further improved and the fluffing of a fabric can be suppressed.

[0170] In the treatment liquid composition for the ink jet pigment textile printing according to the invention, the resin particles are preferably nonionic or cationic resin particles. When the resin particles are nonionic resin particles, a printed textile with excellent color developability and rubbing fastness is obtained particularly when the textile to be printed is cotton. When the resin particles are cationic resin particles, a printed textile with excellent color developability and rubbing fastness is obtained particularly when the textile to be printed is a fabric comprising polyester or polyester mixed yarn.

3.6. Other components

[0171] The treatment liquid composition for ink jet pigment textile printing according to the invention may further include

additional components selected from pH adjusters, antiseptic agents, antifungal agents, antirusts, chelating agents, and the like, which may be added as necessary. As the other components, the same substances illustrated in the ink composition described above may be used.

3.7. Method for preparing treatment liquid composition for ink jet pigment textile printing

[0172] The treatment liquid composition for ink jet pigment textile printing according to the invention can be produced by dispersing and mixing the above-described components by a suitable method. The above-described components may be mixed by stirring, and then filtration is performed in order to remove coarse particles and foreign substances causing clogging, such that a suitable treatment liquid is obtained.

3.8. Physical properties of treatment liquid composition for ink jet pigment textile printing

[0173] When discharged by an ink jet recording head, the treatment liquid composition for ink jet pigment textile printing according to the invention preferably has a surface tension at 20°C of 20 mN/m or more and 40 mN/m or less and more preferably 20 mN/m or more and 35 mN/m or less. For the measurement of the surface tension, the measurement can be performed by, for example, confirming the surface tension when a platinum plate is wetted with an ink in a 20°C environment using an automatic surface tensiometer CBVP-Z (Trade Name, manufactured by Kyowa Interface Science Co., LTD.).

[0174] From the same viewpoint, the viscosity at 20°C of the treatment liquid composition for ink jet pigment textile printing according to the invention is preferably 3 mPa·s or more and 10 mPa·s or less and more preferably 3 mPa·s or more and 8 mPa·s or less. For the measurement of the viscosity, the viscosity in a 20°C environment can be measured using a viscoelasticity testing machine MCR-300 (Trade Name, manufactured by Pysica), for example.

[0175] As described above, the treatment liquid composition for ink jet pigment textile printing according to the invention suppresses the permeation of the ink into a fabric because the nonionic fluorine-based surfactant holds the ink on the surface of the fabric such that sinking of the pigment into the fabric is suppressed. Due to the fact that the surfactant is nonionic, unevenness in color development hardly occurs. Thus, due to the fact that the treatment liquid composition for ink jet pigment textile printing contains the nonionic fluorine-based surfactant, the permeation of the ink into a fabric is controlled, so that a printed textile with excellent color developability, and particularly white color developability, is obtained. The treatment liquid composition set for ink jet pigment textile printing, containing the treatment liquid composition according to the invention and the pigment textile printing ink jet ink composition described above, provides a printed textile having excellent color developability. This is, particularly the case when a two-layer printing method is used in which pigment textile printing is performed using the pigment textile printing ink jet ink composition, and subsequently pigment textile printing is performed using an ink containing a chromatic color pigment.

4. Fabric

[0176] The ink jet pigment textile printing method according to the invention is performed using a fabric. Raw materials configuring the fabric are not particularly limited and the fabric may comprise, for example, natural fibers, such as cotton, hemp, wool, and silk, synthetic fibers, such as polypropylene, polyester, acetate, triacetate, polyamide, and polyurethane, and biodegradable fibers, such as polylactic acid, and the like, and mixed fibers comprising two or more of these may also be used. The fabric may be one obtained by forming the fibers mentioned above into any form of textiles, knit fabrics, nonwoven fabrics, and the like. 1.0 oz (ounce)(28.3 g) or more and 10.0 oz (283.4 g) or less, preferably 2.0 oz (56.7 g) or more and 9.0 oz (255.g) or less, more preferably 3.0 oz (85.0 g) or more and 8.0 oz (226.8 g) or less, and still more preferably 4.0 oz (113.4 g) or more and 7.0 oz (198.4 g) or less. When the mass per unit area of the fabric is within such a range, good recording (textile printing) can be performed. Furthermore, the ink jet pigment textile printing method according to the invention is applicable to a plurality of kinds of fabrics of varying mass per unit area and can achieve good recording.

[0177] In the method of the invention, the fabric can be a fabric containing polyester or polyester mixed yarn. Examples of such a fabric include a polyester fabric and a polyester mixed fabric. Examples of the polyester mixed fabric include a fabric in which polyester is mixed in a proportion of 20% by mass or more, preferably 50% by mass or more, and more preferably 70% by mass or more. The other mixed fibers are not limited and include, for example, cotton. Such a polyester containing fabric has the advantage that moisture, such as sweat, is easy to dry but, on the other hand, in an ink jet textile printing process, the ink easily sinks downward so that the pigment or the resin is hard to fix. In the invention, textile printing is performed using the treatment liquid composition for ink jet pigment textile printing containing the nonionic fluorine-based surfactant described above, and therefore excellent color developability is achieved also in the pigment textile printing to the fabric containing polyester or polyester mixed yarn in which the ink easily sinks downward.

5. Ink jet pigment textile printing method

[0178] Next, each step of the ink jet pigment textile printing method according to the invention is described. The ink jet pigment textile printing method according to the invention includes attaching the pigment textile printing ink jet ink composition to a region where the treatment liquid composition for ink jet pigment textile printing according to the invention is attached by an ink jet method.

5.1. Treatment liquid composition attachment process

[0179] The ink jet pigment textile printing method according to this aspect of the invention includes steps of attaching a treatment liquid composition for ink jet pigment textile printing to a fabric; attaching an ink composition to a fabric; and coagulating the components of the ink composition with the treatment liquid composition in order to improve the color development of a printed textile.

[0180] The treatment liquid composition for ink jet pigment textile printing to be attached to a fabric is suitably the treatment liquid composition for ink jet pigment textile printing of the invention. The treatment liquid composition is preferably attached so that the attachment amount is 0.02 g/cm² or more and 0.5 g/cm² or less and more preferably attached so that the attachment amount is 0.02 g/cm² or more and 0.24 g/cm² or less. By setting the attachment amount of the treatment liquid composition within the range mentioned above, it is easy to apply the treatment liquid composition uniformly to a fabric, and unevenness in the coagulation of an image can be suppressed, and the color development can be improved.

[0181] In the treatment liquid composition attachment step, when the treatment liquid composition contains a polyvalent metal salt, the treatment liquid composition is preferably attached to a fabric so that the attachment amount of the polyvalent metal salt contained in the treatment liquid composition attached to the fabric is 1.6 μmol/cm² or more and 6 μmol/cm² or less and more preferably attached to a fabric so that the attachment amount is 2 μmol/cm² or more and 5 μmol/cm² or less. By attaching the treatment liquid composition so that the attachment amount of the polyvalent metal salt is 1.6 μmol/cm² or more, the color developability of an image to be recorded is improved. By attaching the treatment liquid composition so that the attachment amount of the polyvalent metal salt is 6 μmol/cm² or less, the rubbing fastness of an image to be recorded is improved.

[0182] Examples of methods for attaching the treatment liquid composition to a fabric include, for example, a dipping a fabric into the treatment liquid composition (dip coating), applying the treatment liquid composition by a roll coater or the like (roller coating), ejecting the treatment liquid composition with a spray device or the like (spray coating), ejecting the treatment liquid composition with an ink jet system (ink jet coating), and the like and any of these methods may be used. Herein, when ink jet textile printing is performed using the printer 1 illustrated in the Figure, the treatment liquid composition is preferably attached to the fabric M from the ink jet head 2 by the ink jet coating. When the treatment liquid composition attachment process is performed by the ink jet coating, the treatment liquid composition can be more uniformly attached to the fabric M.

[0183] The ink jet pigment textile printing method according to the invention may include a step of drying the treatment liquid composition attached to a fabric after the treatment liquid composition attachment step. Although the drying of the treatment liquid composition may be performed by natural drying, it is preferred to use drying accompanied by heating as this improves drying speed. When the drying process of the treatment liquid composition involves heating, the heating method is not particularly limited and, for example, any of a heat press method, a normal pressure steam method, a high pressure steam method, and a thermofix method may be used. Examples of the heat source of the heating include infrared rays (lamp), for example.

5.2. Ink composition attachment steps

[0184] The ink composition attachment process includes attaching the pigment textile printing ink jet ink composition described above to a region where the treatment liquid composition for ink jet pigment textile printing is attached to a fabric; and attaching a chromatic color pigment textile printing ink jet ink composition onto the region where the pigment textile printing ink jet ink composition is attached. When the ink composition attachment step includes these two processes, two-layer printing occurs in which an image is formed by the chromatic color pigment textile printing ink jet ink composition on an image formed by the pigment textile printing ink jet ink composition.

[0185] The ink jet pigment textile printing method according to the invention comprises the treatment liquid composition attachment step using the treatment liquid composition for ink jet pigment textile printing of the first aspect of the invention. This contains the nonionic fluorine-based surfactant, and therefore the permeation of an ink attached in the ink-composition attachment steps is suppressed. Moreover, ink components are coagulated by a reaction or an interaction of the cationic compound of the treatment liquid composition and the ink components. Thus, a printed textile having excellent color development properties is obtained.

[0186] In the ink composition attachment steps, when the pigment textile printing ink jet ink composition is a white pigment textile printing ink jet ink composition, the white pigment textile printing ink jet ink composition is preferably attached so that the maximum attachment amount to a fabric is 50 mg/cm² or more and 200 mg/cm² or less, more preferably attached so that the maximum attachment amount to a fabric is 80 mg/cm² or more and 150 mg/cm² or less, and still more preferably attached so that the maximum attachment amount to a fabric is 90 mg/cm² or more and 130 mg/cm² or less. When the maximum attachment amount of the white pigment textile printing ink jet ink composition is as described above, the white color developability is improved. Thus, the color development of the image, particularly when attached to a deep color fabric, is excellent and the image obtained is particularly suitable as a background image. An attachment amount within the range mentioned above is preferable because this ensures that the rubbing fastness of the image is excellent and coagulation unevenness is not conspicuous.

[0187] On the other hand, in the ink composition attachment steps, the maximum attachment amount of the chromatic color pigment textile printing ink jet ink composition can be set to 1 mg/cm² or more and 200 mg/cm² or less. It is preferable to set the maximum attachment amount of the chromatic color pigment textile printing ink jet ink composition to preferably 1 mg/cm² or more and 30 mg/cm² or less, more preferably 2 mg/cm² or more and 25 mg/cm² or less, still more preferably 5 mg/cm² or more and 20 mg/cm² or less, and particularly preferably 7 mg/cm² or more and 15 mg/cm² or less in order that the color developability of an image to be recorded is improved, the drying property of the image is improved, blurring of the image is suppressed, and images, such as pictures and characters, can be recorded on a fabric with good reproducibility.

5.3. Heating step

[0188] The ink jet pigment textile printing method according to the invention preferably includes a step of heating the fabric during the ink composition attachment process. In ink jet textile printing, when a fabric is heated in the ink composition attachment steps, the viscosity and the surface tension decrease due to the fact that the temperature of the ink is high, so that the ink easily uniformly wets and spreads to the fabric and easily permeates into the fabric. Moreover, in the process of the invention, the permeation of the ink is controlled by the nonionic fluorine-based surfactant contained in the ink composition, and therefore the ink uniformly wets and spreads onto the surface of a fabric. Thus, the ink is easily fixed to a fabric, so that the leveling property is improved and the rubbing fastness is excellent in the recorded material obtained. By attaching the ink composition onto a heated fabric, the drying property of the ink can be improved and drying time can be shortened, so that damage to the fabric can be suppressed.

[0189] Examples of a heating method for heating the ink composition given to a fabric include the heating mechanism 6 illustrated in the Figure. Suitable heating mechanisms include a heat press method, a normal pressure steam method, a high pressure steam method, a hot air drying method, a thermofix method, and the like besides the mechanism mentioned above.

[0190] In the heating process, the surface temperature of the heated fabric is preferably 35°C or more and 65°C or less. When the surface temperature of the surface of the fabric is within the range mentioned above, damages to an ink jet head or a fabric can be reduced and the ink easily uniformly wets and spreads to a fabric and easily permeates into a fabric. The heating temperature in this heating process refers to the surface temperature of the heated fabric and can be measured using a noncontact thermometer (Trade Name "IT2-80", manufactured by KEYENCE), for example. The surface temperature of the surface of the heated fabric is preferably 40°C or more and more preferably 45°C or more. The upper limit of the surface temperature is preferably 60°C or less and more preferably 55°C or less.

[0191] The heating time is not particularly limited insofar as the temperature of the fabric surface is within the temperature range mentioned above and, for example, can be set to 5 seconds or more and 1 minute or less and is preferably 10 seconds or more and 30 seconds or less. When the heating time is within the range mentioned above, the fabric can be sufficiently heated while reducing damages to an ink jet head or the fabric.

[0192] Besides the heating step discussed above, the process may include a further step of heating or drying the fabric M after the ink composition attachment process by providing the second heating mechanism on the downstream side in the transporting direction of the fabric M as described with reference to the Figure. In this case, the second heating mechanism is disposed on the downstream side in the transporting direction of the fabric M relative to the heating mechanism 6 of Figure. Thus, the drying property of droplets of the ink attached to the fabric M can be improved. For the second heating mechanism, any one of the mechanisms (for example, drier mechanism and the like) described in the heating mechanism 6 may be used.

[0193] The heating temperature in this case is not limited to the following temperatures and is preferably 100°C or more and 200°C or less, preferably 120°C or more and 160°C or less when the fabric is cotton, and more preferably 100°C or more and 140°C or less when the fabric contains polyester or polyester mixed yarn. A heating temperature is within the range mentioned above promotes a reduction in damage to the fabric and the coating of the resin particles contained in the ink composition. The heating time is not limited to the following time and, for example, can be set to 30 seconds or more and 20 minutes or less and is preferably 2 minutes or more and 7 minutes or less and more preferably

3 minutes or more and 5 minutes or less. Due to the fact that the heating time is within the range mentioned above, the ink can be sufficiently dried while reducing damages to the fabric.

5.4. Operations and Effects

[0194] As described above, in the ink jet pigment textile printing method according to the invention, an ink composition is attached onto the treatment liquid composition for ink jet pigment textile printing according to the invention, and therefore the permeation of an ink attached in the ink-composition adhesion process is suppressed. Moreover, the ink components are coagulated by a reaction or an interaction of the cationic compound of the treatment liquid composition and the ink components. Thus, a printed textile with excellent color developability is obtained.

6. Examples and Comparative Examples

[0195] Hereinafter, the invention is described with reference to Examples but the invention is not limited to Examples.

6.1. Preparation of white ink

[0196] Each component was put into a container so as to have the compositions of Table 1, mixed and stirred with a magnetic stirrer for 2 hours, and further subjected to dispersion treatment in a bead mill filled with zirconia beads 0.3 mm in diameter to be sufficiently mixed. After stirred for 1 hour, filtration was performed using a 5 μ m PTFE membrane filter, so that textile printing ink jet ink compositions were obtained. The numerical values in Table 1 indicate % by mass. Pure water (ion exchanged water) was added so that the total mass of each white ink was 100% by mass.

Table 1

		White ink 1	White ink 2	Color ink 1
Pigment (TiO ₂)		12.0	12.0	
Pigment (C.I. Pigment Blue 15:3)				4.5
Water-dispersible resin (TAKELAC WS-5100)		10.0	10.0	10.0
Organic solvent	Glycerol	5.0	5.0	5.0
	Ethylene glycol	5.0	5.0	5.0
	1,2-hexanediol	1.0	1.0	1.0
Base	KOH	0.2	0.2	0.2
	Triethylamine	1.0	1.0	1.0
Surfactant	FS-300 (Nonionic fluorine-based surfactant)	0.5	-	0.5
	Olefin E1010	-	0.5	-
Water		Balance	Balance	Balance

[0197] In Table 1, the details of components other than the compound name are as follows.

- Water-dispersible resin; TAKELAC WS-5100 (Trade Name, manufactured by Mitsui Chemicals Polyurethanes Inc., Polycarbonate-based urethane resin containing a blocked isocyanate as a crosslinkable group, The numerical values in the tables indicate the solid content of the urethane resin.)
- Fluorine-based surfactant; FS-300 (Trade Name, manufactured by DuPont, Nonionic type)

6.2. Preparation of treatment liquid composition

[0198] Each component was put in a container so as to have the compositions of Tables 2 and 3, and then ion exchanged water was added, so that the total mass was 100% by mass, and then the mixture was mixed and stirred to give treatment liquids.

Table 2

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13
Cationic compound	20	20	20	20	20	20		7	29	20	20	20	20
	Calcium nitrate tetrahydrate												
	Calcium chloride dehydrate												
	Acetic acid						7.0						
	WS-4020												
Resin particles	3.0	3.0	3.0		3.0	3.0	3.0	3.0	3.0	1.0	10.5	3.0	3.0
	Vinyblan 1008 (Cationic resin)												
				3.0									
	Vinyblan 1245L (Nonionic resin)												

(continued)

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13
FS-300 (Nonionic fluorine- based surfactant)	0.5	0.5	0.5	0.5		0.5	0.5	0.5	0.5	0.5	0.5	0.2	0.8
S-241 (Nonionic fluorine- based surfactant)					0.5								
S-221 (Cationic fluorine- based surfactant)													
E1010 (Acetylene- based surfactant)													
Ion exchanged water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Calcium ion concentration (%)	3.4	3.4	3.4	3.4	3.4	3.4	-	1.2	4.9	3.4	3.4	3.4	3.4
Resin solid content concentration (%)	1.5	1.5	1.5	1.2	1.5	1.5	1.5	1.5	1.5	0.5	5.3	1.5	1.5
Printing fabric	PES	Cotton	Mixed yarn	PES	PES	PES	PES	PES	PES	PES	PES	PES	PES
Printing ink	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1	White ink 2	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1
Color developability	A	A	A	B	A	B	B	B	A	B	A	B	A
Rubbing fastness	B	B	B	B	B	B	B	B	B	B	A	B	B

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(continued)

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13
Treatment liquid storageability	A	A	A	A	A	A	A	A	B	A	B	A	B

Table 3

	Ex.14	Ex.15	Ex.16	Ex.17	Ex.18	Ex.19	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6
Cationic compound	Calcium nitrate tetrahydrate		20	20		20		20	20	20	20	20
	Calcium chloride dehydrate	12										
	Acetic acid											
	WS-4020				20							
Resin particles	Vinyblan 1008 (Cationic resin)	3.0	1.2	3.0	3.0	3.0	3.0		3.0	3.0	3.0	3.0
	Vinyblan 1245L (Nonionic resin)											
Surfactant	FS-300 (Nonionic fluorine-based surfactant)	0.5	0.5	1.2	0.5	0.5	0.5	0.5				
	S-241 (Nonionic fluorine-based surfactant)											
	S-221 (Cationic fluorine-based surfactant)									0.5		
	E1010 (Acetylene-based surfactant)											0.5
Ion exchanged water		Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Calcium ion concentration (%)		3.3	5.6	3.4	3.4	0	-	3.4	3.4	3.4	3.4	3.4
Resin solid content concentration (%)		1.5	1.5	6.0	1.5	1.5	1.5	0.0	1.5	1.5	1.5	1.5

(continued)

	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Printing fabric	PES	PES	PES	PES	PES	PES	PES	PES	PES	Cotton	PES	PES
Printing ink	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1	Color ink 1	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1	White ink 1
Color developability	A	A	A	A	B	A	D	D	E	D	D	D
Rubbing fastness	B	B	A	C	A	B	B	D	A	A	B	B
Treatment liquid storageability	A	C	C	C	A	A	A	A	A	A	B	A

[0199] In Tables 2 and 3, the details of components other than the compound name are as follows.

- Cationic compound; WS-4020 (Trade Name, manufactured by SEIKO PMC CORPORATION, Polyamide-epichlorohydrin copolymer)
- Cationic resin; Vinyblan 1008 (Trade Name, manufactured by Nisshin Chemical Co., Ltd., High ability sizing cation-modified article containing modified vinyl acetate as a main component, Solid content of 50%)
- Nonionic resin; Vinyblan 1245L (Trade Name, manufactured by Nisshin Chemical Co., Ltd., Vinyl acetate/Acrylic acid ester, Solid content of 40%)
- Fluorine-based surfactant; FS-300 (Trade Name, manufactured by DuPont, Nonionic type)
- Fluorine-based surfactant; S-241 (Trade Name "Surflon S-241", manufactured by AGC SEIMI CHEMICAL CO., LTD., Nonionic type)
- Fluorine-based surfactant; S-221 (Trade Name "Surflon S-221", manufactured by AGC SEIMI CHEMICAL CO., LTD., Nonionic type)
- Acetylene-based surfactant; E1010 (Trade Name "Olefin E1010", manufactured by Nisshin Chemical Co., Ltd., Acetylene glycol-based surfactant)

6.3. Production of printed matter

6.3.1. Pretreatment

[0200] A commercially-available T-shirt fabric was prepared as a fabric, and then the treatment liquid composition obtained above was uniformly applied thereto using a roller so as to be 18 to 20 g per A4 size. After the application of the treatment liquid, heat treatment was performed at 160°C for 1 minute with a heat press machine. As T-shirts fabrics, the following three kinds of fabrics were used.

T-shirt fabric

[0201]

- Cotton (manufactured by Hanes, Heavyweight black, 100% cotton)
- PES (glimmer ACTIVE WEAR, 3.5 oz, Dry T-shirt, Black, 100% polyester)
- Mixed yarn (Printstar, 4.6 oz, Honeycomb mesh T-shirt, Black, Cotton/Polyester:45/55)

6.3.2. Printing of white ink

[0202] A white ink was applied to the fabrics after the pretreatment by an ink jet method using an ink jet printer (PX-G930: manufactured by Seiko Epson Corp.). As a printing pattern, printing was performed under the conditions where the resolution was set to 1440 × 1440 dpi and solid printing was overlapped 4 times to obtain fabrics printed with the white ink. Thereafter, in order to confirm the whiteness, the fabrics after the printing were heat treated at 160°C for 1 minute with a heat press machine to fix the white ink to the fabrics to thereby obtain fabrics printed with the white ink.

6.4. Evaluation test

[0203] The obtained fabrics were evaluated for whiteness and rubbing resistance.

6.4.1. Evaluation of color developability

[0204] For the fabrics after the printing, the L* value in the CIE/L*a*b* color system was measured using a commercially-available colorimeter (Product Name "Gretag Macbeth Spectrolino", manufactured by X-Rite), and then determined based on the following evaluation criteria. When the evaluation result is determined to be B or higher, it can be said that the effects of the invention of this application are obtained.

Evaluation criteria of white ink

[0205]

A: $80 \leq L^*$

B: $75 \leq L^* < 80$

C: $70 \leq L^* < 75$

D: $65 \leq L^* < 70$

E: $L^* < 65$

6.4.2. Evaluation of rubbing fastness

[0206] To the fabrics after the printing, a color fastness test to rubbing was carried out using an I type (clock meter) testing machine according to a drying test specified in ISO-105 X12. The evaluation was performed using a contamination gray scale. The evaluation criteria were as follows and the results are given in the tables.

Evaluation criteria

[0207]

A: Rubbing fastness is Class 4 or higher.

B: Rubbing fastness is Class 3 or higher and less than Class 4.

C: Rubbing fastness is Class 2 or higher and less than Class 3.

D: Rubbing fastness is less than Class 2.

6.4.3. Evaluation of treatment liquid storageability

[0208] The obtained treatment liquid was charged into a sample bottle, and then allowed to stand at 60°C for 10 days. Thereafter, the presence or absence of the generation of foreign substances and printed matter were visually confirmed, and then evaluated based on the following evaluation criteria.

Evaluation criteria

[0209]

A: No foreign substances were generated and the printed matter also had no problem.

B: Some foreign substances were observed but the printed matter had no problem.

C: Foreign substances were observed and the printed matter was somewhat changed in quality.

6.5. Evaluation results

[0210] All Comparative Examples 1 to 6 outside the scope of the invention had the results that the color developability was low. First, Comparative Example 1 containing no cationic compounds had the result that the color developability was low. Comparative Example 2 containing the cationic compound but containing no resin particles had the result that the color developability and the rubbing fastness were low. Comparative Example 3 containing no nonionic fluorine-based surfactant had the result that the color developability was the lowest. Comparative Example 4 which had the combination of Comparative Example 3 and which was printed to cotton had the result that the color developability was slightly higher than that of Comparative Example 3 but was low. Comparative Examples 5 and 6 containing surfactants other than the nonionic fluorine-based surfactant had the results that the color developability was low.

[0211] Examples 1 to 19 had the results that the color developability was higher than that of Comparative Examples 1 to 6. In Example 1, not only the color developability but the rubbing fastness was high to the PES used as the fabric and the treatment liquid storageability was also high. Examples 2 and 3 which had the combination of Example 1 and which were printed to the other fabrics had the same result as that of Example 1.

[0212] In Example 4 containing a nonionic resin as resin particles, the color developability slightly decreased. Example 5 containing a nonionic fluorine-based surfactant different from that of Example 1 as the surfactant had the result that all the evaluations were high similarly to Example 1.

[0213] In Example 6 containing a white ink different from that of Example 1, the surfactant of the ink was an acetylene-based surfactant, and therefore the color developability slightly decreased. In Example 7 containing acetic acid as a cationic compound unlike Example 1, the color developability slightly decreased.

[0214] In Example 8 in which the content of the cationic compound was lower than that of Example 1, the color developability slightly decreased. On the other hand, Example 9 in which the content of the cationic compound is higher than that of Example 1 had the result that the treatment liquid storageability slightly decreased and Example 15 having a much higher content had the result that the treatment liquid storageability was low.

[0215] In Example 10 in which the content of the resin particles was lower than that of Example 1, the color developability

slightly decreased. On the other hand, Example 11 in which the content of the resin particles was higher than that of Example 1 had the result that the treatment liquid storageability slightly decreased and Example 16 having a much higher content had the result that the treatment liquid storageability was low.

[0216] In Example 12 in which the content of the nonionic fluorine-based surfactant was lower than that of Example 1, the color developability slightly decreased. On the other hand, Example 13 in which the content of the nonionic fluorine-based surfactant was higher than Example 1 had the result that the treatment liquid storageability slightly decreased and Example 17 having a much higher content had the result that the rubbing fastness and the treatment liquid storageability were low.

[0217] Also Example 14 containing a polyvalent metal salt different from that of Example 1 had the result that all the evaluations were high similarly to Example 1.

[0218] In Example 18 containing a cationic compound different from that of Example 1, the color developability slightly decreased as compared with Example 1 but the rubbing fastness became high. Also Example 19 containing a color ink had the same result as that of Example 1.

[0219] The invention is not particularly limited to the embodiments described above and can be variously modified. For example, the invention includes the substantially same structures (e.g., structures with the same function(s), method(s), and result(s) or structures with the same object(s) and effect(s)) as the structures described in the embodiments. The invention also includes structures in which non-essential portions of the structures described in the embodiments are replaced. The invention also includes structures that can demonstrate the same operational effects or structures that can achieve the same objects as those in the structures described in the embodiments. The invention also includes structures in which known techniques are added to the structures described in the embodiments.

Claims

1. A treatment liquid composition for ink jet pigment textile printing for attachment to a fabric in ink jet pigment textile printing, the treatment liquid composition for ink jet pigment textile printing comprising:

a cationic compound;
a nonionic fluorine-based surfactant;
a resin particle; and
water.

2. The treatment liquid composition for ink jet pigment textile printing according to Claim 1, wherein the fabric comprises polyester or polyester mixed yarn.

3. The treatment liquid composition for ink jet pigment textile printing according to claim 1 or claim 2, wherein the cationic compound is a polyvalent metal salt, an organic acid, or a cationic resin.

4. The treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 3, wherein the cationic compound contains either calcium nitrate or calcium chloride.

5. The treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 4, wherein the nonionic fluorine-based surfactant has an HLB value within a range of 6 or more and 15 or less.

6. The treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 5, wherein the nonionic fluorine-based surfactant has a polyoxyethylene group and an alkyl fluoride group.

7. The treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 6, wherein the resin particle is a nonionic or cationic resin particle.

8. The treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 7, wherein the treatment liquid composition does not contain a colorant.

9. An ink jet pigment textile printing set comprising:

the treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 8; and
a pigment textile printing ink jet ink composition containing a pigment, a resin particle, and water.

10. The ink jet pigment textile printing set according to Claim 9, wherein the resin particle contained in the pigment textile printing ink jet ink composition contains a polycarbonate-based urethane resin.

5 11. The ink jet pigment textile printing set according to Claim 9 or claim 10, wherein the pigment textile printing ink jet ink composition further contains a fluorine-based surfactant.

10 12. An ink jet pigment textile printing method comprising:
attaching a pigment textile printing ink jet ink composition to a region where the treatment liquid composition for ink jet pigment textile printing according to any one of claims 1 to 8 is attached by an ink jet method.

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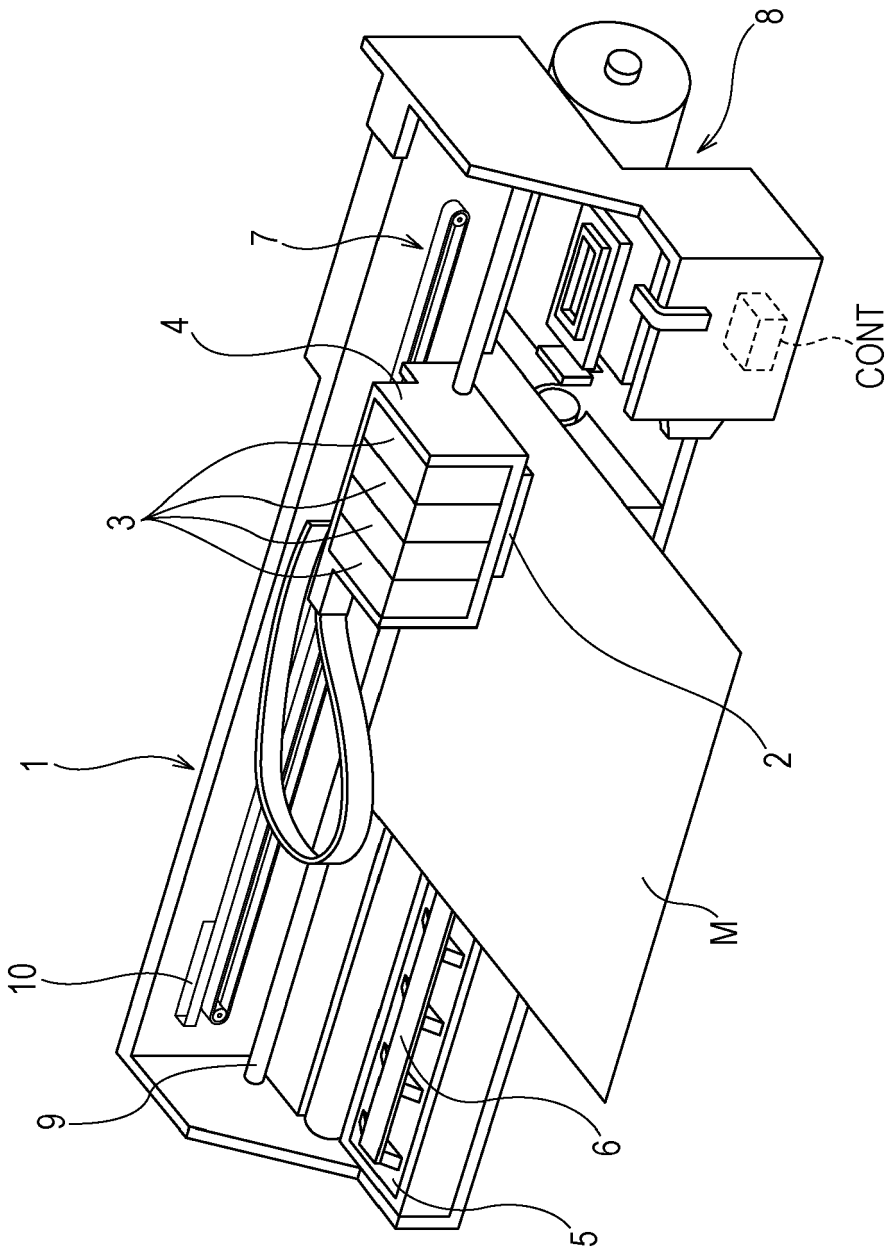
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FIGURE





EUROPEAN SEARCH REPORT

Application Number
EP 19 15 4655

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2016/060810 A1 (SAITO TORU [JP] ET AL) 3 March 2016 (2016-03-03) * paragraph [0032] * * paragraph [0067] * * paragraphs [0071] - [0072] * * examples 1-12 * * table 1 * * claim 1 *	1,3,4,6,8-12	INV. D06P3/34 D06P5/30 D06P1/52 D06P1/673
X,P	----- EP 3 421 553 A1 (SEIKO EPSON CORP [JP]) 2 January 2019 (2019-01-02) * paragraph [0009] * * paragraph [0073] * * paragraphs [0077] - [0079] * * paragraph [0085] * * paragraphs [0198] - [0199] * * examples 1-24 * * tables 1-3 * * claim 1 * -----	1-5,7,8	
			TECHNICAL FIELDS SEARCHED (IPC)
			D06P
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 25 June 2019	Examiner Rella, Giulia
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	

EPO FORM 1503 03/82 (P04C01)

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

EP 19 15 4655

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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25-06-2019

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