



US 20160060810A1

(19) **United States**

(12) **Patent Application Publication**  
**SAITO et al.**

(10) **Pub. No.: US 2016/0060810 A1**

(43) **Pub. Date: Mar. 3, 2016**

(54) **TEXTILE PRINTING INK SET AND IMPRINTING METHOD**

**Publication Classification**

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(51) **Int. Cl.**  
**D06P 5/30** (2006.01)  
**D06P 1/52** (2006.01)

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(52) **U.S. Cl.**  
CPC ..... **D06P 5/30** (2013.01); **D06P 1/5285** (2013.01); **D06P 1/525** (2013.01)

(21) Appl. No.: **14/840,577**

(57) **ABSTRACT**

(22) Filed: **Aug. 31, 2015**

A textile printing ink set includes a pre-treatment liquid containing a flocculant; and an aqueous ink jet ink composition, in which the aqueous ink jet ink composition contains resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid.

(30) **Foreign Application Priority Data**

Sep. 1, 2014 (JP) ..... 2014-177500

## TEXTILE PRINTING INK SET AND IMPRINTING METHOD

### BACKGROUND

**[0001]** 1. Technical Field

**[0002]** The present invention relates to a textile printing ink set and an imprinting method.

**[0003]** 2. Related Art

**[0004]** In an ink jet recording method, a high definition image can be recorded with a relatively simple device, and the ink jet recording method has rapidly developed in various fields. Among them, textile printing ink has been reviewed in various ways. For example, JP-A-2009-30014 discloses a method of manufacturing a textile printed product including a step of applying a pre-treatment agent containing multivalent metal salt in a printed portion on printed matter and a step of printing predetermined textile printing ink jet ink by an ink jet recording method for the purpose of providing a textile printing ink jet ink that can realize satisfactory wash fastness and friction fastness and also satisfactory concealing properties even when being used on a dark colored fabric.

**[0005]** However, in a method of flocculating a resin in an ink composition using the pre-treatment agent described above, a resin flocculates in an early stage before the resin comes into contact with a recording medium, and thus the adhesiveness decreases. In addition, in a method in which a pre-treatment agent is not used, a coloring material penetrates the recording medium, and thus the color developing properties decrease.

### SUMMARY

**[0006]** An advantage of some aspects of the invention is to provide a textile printing ink set having excellent color developing properties and adhesiveness, and an imprinting method using the textile printing ink set.

**[0007]** The inventors of the invention diligently studied in order to solve the problems described above. As a result, the inventors found that the problems can be solved by using a predetermined resin so as to complete the invention.

**[0008]** That is, the invention is as follows.

**[0009]** [1] A textile printing ink set including: a pre-treatment liquid that contains a flocculant; and an aqueous ink jet ink composition, in which the aqueous ink jet ink composition contains resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid.

**[0010]** [2] The textile printing ink set described in [1], in which the resin fine particles (B) include at least one of an emulsifier dispersion-type resin or a nonionic resin.

**[0011]** [3] The textile printing ink set described in [1] or [2], in which the resin fine particles (A) include a self-dispersion-type anionic resin.

**[0012]** [4] The textile printing ink set described in any one of [1] to [3], in which the resin fine particles (A) include a self-dispersion-type urethane resin, and the resin fine particles (B) include an emulsifier dispersion-type acryl resin.

**[0013]** [5] The textile printing ink set described in any one of [1] to [4], in which the resin fine particles (A) include an anionic urethane resin, and the resin fine particles (B) include a nonionic urethane resin.

**[0014]** [6] The textile printing ink set described in any one of [1] to [5], in which the aqueous ink jet ink composition further contains a white pigment.

**[0015]** [7] The textile printing ink set described in any one of [1] to [6], in which a total content of solid contents of the resin fine particles (A) and the resin fine particles (B) is in a range of 8.0% by mass to 20% by mass with respect to a total amount of the aqueous ink jet ink composition, a content of the solid content of the resin fine particles (A) is in a range of 5.0% by mass to 12% by mass, with respect to a total amount of the aqueous ink jet ink composition, and a content of the solid content of the resin fine particles (B) is in a range of 3.0% by mass to 10% by mass with respect to a total amount of the aqueous ink jet ink composition.

**[0016]** [8] The textile printing ink set described in any one of [1] to [7], in which a content of the solid content of the resin fine particles (A) is greater than that of the solid content of resin fine particles (B).

**[0017]** [9] An imprinting method, including: adhering a pre-treatment liquid contained in the textile printing ink set described in any one of [1] to [8] to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set described in any one of [1] to [8] from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.

**[0018]** [10] The imprinting method described in [9], in which after the adhering of the pre-treatment liquid, in a state in which 30% by mass or more of a volatile component of the pre-treatment liquid adhered to the fabric remains, the discharging and adhering of the aqueous ink jet ink composition is performed.

**[0019]** [11] The imprinting method described in [9] or [10], further including: heating the fabric after the discharging and adhering of the aqueous ink jet ink composition, in which, in the heating of the fabric, a surface of the fabric to which the aqueous ink jet ink composition is adhered is not pressurized.

### DESCRIPTION OF EXEMPLARY EMBODIMENTS

**[0020]** Hereinafter, the invention is described with reference to embodiments to realize the invention (hereinafter, referred to as “embodiments”). However, the invention is not limited to the embodiments, and various modifications are possible without departing from the gist of the invention.

#### Textile Printing Ink Set

**[0021]** The textile printing ink set according to the embodiment includes a pre-treatment liquid that contains a flocculant and an aqueous ink jet ink composition, and the aqueous ink jet ink composition (hereinafter, simply referred to as “ink composition”) contains resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid.

**[0022]** In the related art, in a method of causing the resin in the ink composition by using the pre-treatment agent to flocculate, it is possible to prevent the resin in the ink composition from flocculating and a pigment from penetrating fabric fibers, and thus color developing properties can be improved, but the resin flocculates in an early stage before the resin comes into contact with a recording medium, and thus the adhesiveness decreases. On the contrary, the textile printing

ink set according to the embodiment includes the ink composition including the resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and the resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid, and thus the adhesiveness is improved while high color developing properties are maintained.

**[0023]** In addition, in order to increase the imprinting speed, the ink composition is adhered to the fabric without waiting until the pre-treatment liquid has dried, and thus a decrease in the adhesiveness becomes significant. However, if the textile printing ink set according to the embodiment is used, the adhesiveness can be improved even if the speed is increased.

**[0024]** Further, at the time of imprinting, the ink composition is fixed while the texture of the fabric remains, and thus even if the surface to which the ink composition of the fabric is adhered is heated without being pressurized, the decrease in the adhesiveness described above becomes significant compared with that in a case of being pressurized. However, if the textile printing ink set according to the embodiment is used, even if the imprinting method described above is used, adhesiveness can be improved.

#### Pre-Treatment Liquid

**[0025]** The pre-treatment liquid contains a flocculant. If the flocculant in the pre-treatment liquid interacts with the ink composition, the ink composition is thickened or insolubilized. Accordingly, the landing interference and the bleeding of the ink composition adhered thereafter can be prevented, and thus lines, fine images, or the like can be painted homogeneously. Also, it is possible to prevent the coloring material from penetrating into fabric fibers, and thus color developing properties are also improved. The flocculant is not particularly limited, and, for example, polyvalent metal salt and organic acid are included. Among these, it is preferable that the pre-treatment liquid includes polyvalent metal salt. If the pre-treatment liquid including the polyvalent metal salt is used, the flocculation effect of resin fine particles (A) is improved, and color developing properties tend to be further improved.

#### Polyvalent Metal Salt

**[0026]** The polyvalent metal salt is not particularly limited, but, for example, polyvalent metal salt of inorganic acid and polyvalent metal salt of organic acid are preferable. The polyvalent metal salt is not particularly limited, and, for example, salts of alkaline earth metals (for example, magnesium and calcium) in Group 2 of the periodic table and earth metal (for example, aluminum), transition metal (for example, lanthan) in Group 3 of the periodic table, and lanthanides (for example, neodymium) in Group 13 of the periodic table are included. As the polyvalent metal salt, carboxylate (formate, acetate, and benzoate), sulfates, nitrates, chlorides, and thiocyanate are preferable. Among them, calcium salt or magnesium salt of carboxylic acid (formic acid, acetic acid, benzoic acid, and the like), calcium salt or magnesium salt of sulfate, calcium salt or magnesium salt of nitric acid, calcium chloride, magnesium chloride, and calcium salt or magnesium salt of thiocyanic acid are preferably included. In addition, the polyvalent metal salts may be used singly, or two or more types thereof may be used in combination.

#### Organic Acid

**[0027]** The organic acid is not particularly limited, but for example, acetic acid, phosphoric acid, oxalic acid, malonic acid, and citric acid are included. Among them, univalent or bivalent or more carboxylic acid is preferable. If the carboxylic acid is included, the flocculation effect of the resin fine particles (A) is improved, and further the color developing properties tends to be more excellent. In addition, the organic acids may be used singly, or two or more types thereof may be used in combination.

**[0028]** The content of the flocculant is preferably in the range of 1.0 parts by mass to 15 parts by mass, more preferably in the range of 2.5 parts by mass to 12.5 parts by mass, and still more preferably 4.0 parts by mass to 10.0 parts by mass with respect to the total amount (100 parts by mass) of the pre-treatment liquid. If the content of the flocculant is in the range described above, the flocculation effect of the resin fine particles (A) is more improved, and the color developing properties tend to be more excellent.

**[0029]** The pre-treatment liquid may include other components, if necessary. The other components are not particularly limited, but, for example, surfactants, solvents, and resins are included.

#### Surfactant

**[0030]** The pre-treatment liquid preferably contains a surfactant. The surfactant is not particularly limited, but, for example, an acetylene glycol-based surfactant, a fluorine-based surfactant, and a silicone-based surfactant are included.

**[0031]** The acetylene glycol-based surfactant is not particularly limited, but, for example, at least one selected from alkylene oxide adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol and alkylene oxide adducts of 2,4-dimethyl-5-decyne-4-ol and 2,4-dimethyl-5-decyne-4-ol is preferable. The commercially available product of the acetylene glycol-based surfactant is not particularly limited, and, for example, Olfine 104 series or E series such as Olfine E1010 (Product names manufactured by Air Products Japan, Inc.), and Sufynol 465 or Sufynol 61 (Product names manufactured by Nissin Chemical Industry Co., Ltd.) are included. The acetylene glycol-based surfactants may be used singly, or two or more types thereof may be used in combination.

**[0032]** The fluorine-based surfactant is not particularly limited, but, for example, perfluoroalkyl sulfonate, perfluoroalkyl carboxylate, perfluoroalkyl phosphate ester, a perfluoroalkyl ethylene oxide adduct, perfluoroalkyl betaine, and a perfluoroalkyl amine oxide compound are included. The commercially available product of the fluorine-based surfactant is not particularly limited, but S-144 and S-145 (manufactured by Asahi Glass Co., Ltd.); FC-170C, FC-430, FLUORAD-FC4430 (manufactured by 3M); FSO, FSO-100, FSN, FSN-100, FS-300 (manufactured by Dupont); and FT-250 and 251 (manufactured by Neos Company Limited), and the like are included. The fluorine-based surfactants may be used singly, and two or more types thereof may be used in combination.

**[0033]** As the silicone-based surfactant, polysiloxane compound, polyether-modified organosiloxane are included. The commercially available product of the silicone-based surfactant is not particularly limited, and for example, BYK-306, BYK-307, BYK-333, BYK-341, BYK-345, BYK-346, BYK-347, BYK-348, and BYK-349 (Product names manu-

factured by BYK Japan KK), and 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 (Product names manufactured by Shin-Etsu Chemical Co., Ltd.) are included. The silicone-based surfactants may be used singly, and two or more types thereof may be used in combination.

**[0034]** The content of the surfactant is preferably in the range of 0.050 parts by mass to 2.5 parts by mass, and more preferably in the range of 0.10 parts by mass to 3.0 parts by mass with respect to the total amount (100 parts by mass) of the pre-treatment liquid. If the content of the surfactant is in the range described above, the wettability of the pre-treatment liquid adhered to the recording medium tends to be more enhanced.

#### Solvent

**[0035]** The solvent is not particularly limited, but, for example, an organic solvent or water can be used.

**[0036]** As water, for example, pure water such as ion-exchanged water, ultrafiltration water, reverse osmosis water, and distilled water, and water such as ultrapure water from which ionic impurities are removed to the greatest extent can be used. In addition, if water sterilized by the irradiation of ultraviolet rays or the addition of hydrogen peroxide is used, if the pre-treatment liquid is stored for a long time, the generation of molds and bacteria can be prevented. Accordingly, the storage stability is more improved.

**[0037]** The organic solvent is not particularly limited, and, for example, hydrocarbon-based solvents such as toluene, hexane, cyclohexane, benzene, octane, and isooctane; ester solvents such as ethyl acetate, butyl acetate, and  $\gamma$ -butyrolactone; ketone solvents such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; alcohol-based solvents such as methanol, ethanol, propanol, isopropanol, and butanol; halogenated solvents such as dichloroethane and chloroform; ether-based solvents such as diethyl ether, and tetrahydrofuran; amide-based solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, 2-pyrrolidone, N-methyl- $\epsilon$ -caprolactam, and hexamethylphosphoramide, glycerine, triethylene glycol, triethylene glycol monobutyl ether, and water soluble organic solvents are included.

**[0038]** The content of the solvent is preferably in the range of 0.050 parts by mass to 7.5 parts by mass, and more preferably in the range of 0.10 parts by mass to 5.0 parts by mass with respect to the total amount (100 parts by mass) of the pre-treatment liquid. If the content of the solvent is in the range described above, the wettability of the pre-treatment liquid which is adhered to the recording medium tends to be improved.

#### Resin

**[0039]** The pre-treatment liquid may include the resin. The resin included in the pre-treatment liquid is not particularly limited, and for example, an acrylic resin, a styrene-acrylic resin, a urethane resin, a POI olefin resin, a polyamide resin, an epoxy resin, a vinyl chloride resin, a vinyl acetate resin, and the like are included. As the resin, a type which is soluble in water is possible, but in view of preventing the increase of the viscosity of the pre-treatment liquid at the time of adding the resin, an emulsion-type resin is preferably used. The

resins caused to be in an emulsion state by a known method in the art for the emulsification can be used.

**[0040]** The commercially available product of the acrylic resin is not particularly limited, but, for example, Mowinyl 952B and 718A (Product names manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.), Nipol LX872 and LX874 (Product names manufactured by Zeon Corporation), are included.

**[0041]** The styrene-acrylic resin is not particularly limited, but, for example, JONCRYL 7100 and 390 (Product names manufactured by BASF Corporation), and Mowinyl 966A and 975N (Product names manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) are included.

**[0042]** The urethane-based resin is not particularly limited, and, for example, Superflex 460 and 840 (Product names manufactured by DKS Co., Ltd.) are included.

**[0043]** The vinyl acetate resin is not particularly limited, and, for example, Vinyblan 1245L and 1225 (Product names manufactured by Nissin Chemical Industry Co., Ltd.), and Mowinyl 50M, 350, 352 (Product names manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) are included.

**[0044]** The friction resistance and the washing resistance of the coating film after the printing can be more enhanced by adding the resin to the pre-treatment agent.

**[0045]** The content of the resin is preferably in the range of 0.050 parts by mass to 2.5 parts by mass, and more preferably in the range of 0.10 parts by mass to 5.0 parts by mass with respect to the total amount (100 parts by mass) of the pre-treatment liquid. If the content of the resin is in the range described above, the texture of the obtainable recorded product is more improved.

#### Aqueous Ink Jet Ink Composition

**[0046]** The aqueous ink jet ink composition contains the resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and the resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid. Herein, the expression "flocculate" refers to determining flocculation by a "determination method of flocculation" described in examples. The expression "do not flocculate" refers to determining no flocculation by the "determination method of flocculation" described in the examples.

#### Resin Fine Particles (A)

**[0047]** The resin fine particles (A) flocculate by being mixed with the pre-treatment liquid. The resin fine particles (A) are not particularly limited, and, for example, products which are the self-dispersion-type resin or the anionic resin and which flocculate by being mixed with the pre-treatment liquid are included. Among them, the self-dispersion-type anionic resin, the self-dispersion-type urethane resin, and the anionic urethane resin are preferable. If the resin fine particles (A) are included, the color developing properties of the resin fine particles (A) tend to be improved. In addition, the expression "self-dispersion-type resin" refers to a resin that does not need dispersion assistance and which is self-dispersed. In addition, the expression "anionic resin" refers to a resin that has negative electric charge in the entire resin.

**[0048]** The resin fine particles (A) are preferably a resin emulsion. The self-dispersion-type anionic resin, the self-dispersion-type urethane resin, and the anionic urethane resin are not particularly limited, but, for example, a polyether-

based urethane resin including an ether linkage in a main chain, a polyester-based urethane resin including an ester bond in a main chain, and a polycarbonate-type urethane resin including a carbonate bond in a main chain are included. In addition, the commercially available product is not particularly limited, and for example, Sun Cure 2710 and 2715 (Product names manufactured by The Lubrizol Corporation), Permarin UA-150 (Product name manufactured by Sanyo Chemical Industries, Ltd.), Takelac (Registered Trademark), and WS-6021 and W-6061 (Product names manufactured by Mitsui Chemicals, Inc.) are included.

**[0049]** A content of the solid content of the resin fine particles (A) is preferably in the range of 1.0% by mass to 20% by mass, more preferably in the range of 2.0% by mass to 15% by mass, still more preferably in the range of 3.0% by mass to 15% by mass, and particularly more preferably in the range of 5.0% by mass to 12% by mass with respect to the total amount of the aqueous ink jet ink composition. If the content of the solid content of the resin fine particles (A) is 1.0% by mass or greater, and the color developing properties tend to be more improved. In addition, if the content of the solid content of the resin fine particles (A) is 20% by mass or less, the ink viscosity tends not to be excessively great. Particularly, if the content of the solid content of the resin fine particles (A) is in the range of 5.0% by mass to 12% by mass, when being used as the ink composition having the white pigment, the color developing properties are excellent, and the ink viscosity tends not to be excessively high.

#### Resin Fine Particles (B)

**[0050]** The resin fine particles (B) do not flocculate by being mixed with the pre-treatment liquid. Accordingly, the resin fine particles (B) have a function of sticking between the pigment and the fabric, between the resin fine particles (A) and the fabric, and between the pigment and the resin fine particles (A), such that the adhesiveness tends to be more improved. The resin fine particles (B) are not particularly limited, and, for example, the resin emulsion such as the emulsifier dispersion-type resin and the nonionic resin are included. If the resin fine particles (B) include at least one of the emulsifier dispersion-type resin and the nonionic resin, the adhesiveness tends to be more improved. Here, the expression "emulsifier dispersion-type resin" refers to a resin which requires a dispersion assistant (emulsifier), and is dispersed by a dispersion assistant. In addition, the "nonionic resin" refers to a resin which includes a resin having a functional group that is not ionized by electrolytic dissociation.

**[0051]** The emulsifier dispersion-type resin is not particularly limited, but, for example, an emulsifier dispersion-type acryl resin is included. The nonionic resin is not particularly limited, and, for example, the nonionic urethane resin is included.

**[0052]** The emulsifier dispersion-type acryl resin is not particularly limited, and, for example, products obtained by polymerizing a (meth)acrylic monomer such as (meth)acrylic acid and (meth)acrylic acid ester, or products obtained by copolymerizing the (meth)acrylic monomer and another monomers such as styrene are included. The commercially available product of the emulsifier dispersion-type acryl resin is not particularly limited, and, for example, Mowinyl 966A (Product name manufactured by Nippon Synthetic Chemical Industry Co., Ltd.), Microgel E-1002 and Microgel E-5002 (Product names manufactured by Nippon Paint Co., Ltd.), Bonkote 4001 and Bonkote 5454 (Product names manufac-

ured by DIC Corporation), SAE1014 (Product name manufactured by Zeon Corporation), Saibinol SK-200 (Product name manufactured by SAIDEN CHEMICAL INDUSTRY CO., LTD.), NK Binder R-5HN (Product name manufactured by Shin-Nakamura Chemical Co., Ltd., solid content: 44%), and Vinyblan 2650 (Product name manufactured by Nissin Chemical Industry Co., Ltd.) are included.

**[0053]** The content of the solid content of the resin fine particles (B) is preferably in the range of 1.0% by mass to 20% by mass, more preferably in the range of 2.0% by mass to 15% by mass, and still more preferably in the range of 3.0% by mass to 10% by mass with respect to the total amount of the aqueous ink jet ink composition. If the content of the solid content of the resin fine particles (B) is 1.0% by mass or more, the adhesiveness tends to be more improved. In addition, if the content of the solid content of the resin fine particles (B) is 20% by mass or less, the color developing properties tend to be more improved. Particularly, if the content of the solid content of the resin fine particles (B) is in the range of 3.0% by mass to 10% by mass, when the resin fine particles (B) are used as the ink composition having a white pigment, both of the adhesiveness and the color developing properties are excellent, and the obtainable recording product tends to be more excellent as an undercoat of a colored ink composition.

**[0054]** The combination of the resin fine particles (A) and the resin fine particles (B) is not particularly limited, but, for example, a combination of the resin fine particles (A) including the self-dispersion-type urethane resin and the resin fine particles (B) including an emulsifier dispersion-type acryl resin, or a combination of the resin fine particles (A) including an anionic urethane resin, and the resin fine particles (B) including the nonionic urethane resin is preferable. If the combination is used, the color developing properties and the adhesiveness tend to be more improved.

**[0055]** The total content of the solid contents of the resin fine particles (A) and the resin fine particles (B) is preferably in the range of 1.0% by mass to 30% by mass, more preferably in the range of 2.0% by mass to 25% by mass, still more preferably in the range of 3.0% by mass to 20% by mass, and particularly more preferably in the range of 8.0% by mass to 20% by mass with respect to the total amount of the aqueous ink jet ink composition. If the content of the solid contents of the resin fine particles (A) and the resin fine particles (B) is 1.0% by mass or greater, the color developing properties and the adhesiveness tend to be more improved. In addition, if the content of the solid content of the resin fine particles (A) and the resin fine particles (B) is 30% by mass or less, the texture of the obtainable recording product tends to be more improved. Particularly, if the content of the solid contents of the resin fine particles (A) and the resin fine particles (B) is 8.0% by mass to 15% by mass, when the resin fine particles (A) and the resin fine particles (B) are used as the ink composition having the white pigment, both of the adhesiveness and the color developing properties are excellent, and the obtainable recording product tends to be more excellent as an undercoat of a colored ink composition.

**[0056]** The content of the solid content of the resin fine particles (A) is preferably greater than that of the solid content of the resin fine particles (B), since the color developing properties are improved. In addition, the ratio of the content of the solid content of the resin fine particles (A) to the content of the solid content of the resin fine particles (B) (resin fine particles (A)/resin fine particles (B)) is preferably 0.50 or more, more preferably 1.0 or more, still more preferably

greater than 1.0, further still more preferably 1.1 or greater, and particularly preferably 1.5. If the ratio (resin fine particles (A)/resin fine particles (B)) is 0.50 or greater, the color developing properties tend to be more improved. In addition, the ratio of the content of the solid content of the resin fine particles (A) to the content of the solid content of the resin fine particles (B) (resin fine particles (A)/resin fine particles (B)) is preferably 5.0 or lower, more preferably 4.0 or lower, still more preferably 3.0 or lower, and particularly preferably 2.0 or lower. If the ratio (resin fine particles (A)/resin fine particles (B)) is 5.0 or lower, the adhesiveness tends to be more improved.

#### Pigment

**[0057]** The ink composition may contain the pigment. The pigment is not particularly limited, and, for example, the following are included.

**[0058]** The carbon black used in the black ink is not particularly limited, and, for example, No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100, No. 2200B, and the like (Product names manufactured by Mitsubishi Chemical Corporation), Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, Raven 700, and the like (Product names manufactured by Carbon Columbia), 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 (Product names manufactured by CABOT JAPAN K.K.), and 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 (Product names manufactured by Degussa AG) are included.

**[0059]** The pigment (white pigment) used in white ink is not particularly limited, and, for example, C.I. Pigment White 6, 18, 21, titanium oxide, zinc oxide, zinc sulfide, antimony oxide, zirconium oxide, white hollow resin particles, and polymer particles are included.

**[0060]** The pigment used in yellow ink is not particularly limited, but, for example, 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 are included.

**[0061]** The pigment used in the magenta ink is not particularly limited, but, for example, 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, 48:2, 48:5, 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, and C.I. Pigment Violet 19, 23, 32, 33, 36, 38, 43, and 50 are included.

**[0062]** The pigment used in the cyan ink is not particularly limited, and, for example, 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, and C.I. Vat Blue 4 and 60 are included.

**[0063]** In addition, the other pigments are not particularly limited, but, for example, C.I. Pigment Green 7 and 10, C.I. Pigment Brown 3, 5, 25, and 26, and C.I. Pigment Orange 1, 2, 5, 7, 13, 14, 15, 16, 24, 34, 36, 38, 40, 43, and 63 are included.

**[0064]** Among these, it is preferable that the ink composition further includes white pigment. If white pigment is further included, both of the adhesiveness and the color devel-

oping properties are excellent, and the obtainable recording product tends to have better texture as an undercoat of a colored ink composition.

**[0065]** The content of the pigment is preferably in the range of 2.0 parts by mass to 15 parts by mass, more preferably in the range of 6.0 parts by mass to 10 parts by mass with respect to the total amount (100 parts by mass) of the ink composition. If the content of the pigment is in the range described above, the color developing properties tend to be more improved.

#### Solvent

**[0066]** The ink composition may contain a solvent. As the solvent, among the products described in the pre-treatment liquid, water and a water-soluble solvent are exemplified. The content of water is preferably in the range of 50 parts by mass to 80% by mass, more preferably in the range of 55 parts by mass to 75% by mass, and still more preferably in the range of 60 parts by mass to 70% by mass with respect to the total amount of the ink composition. If the aqueous ink composition of which the content of water is in the range described above is used, the viscosity of the ink can be decreased and there is less influence on the combustibility of the organic solvent. Therefore, the invention is advantageous.

#### Surfactant

**[0067]** The ink composition may include a surfactant. As the surfactant, products described as the pre-treatment liquid are exemplified.

**[0068]** The content of the surfactant is preferably in the range of 0.10 parts by mass to 1.0 parts by mass, and more preferably in the range of 0.10 parts by mass to 0.50 parts by mass with respect to the total amount of the ink composition. If the content of the surfactant is in the range described above, the wettability tends to be more improved.

#### Other Components

**[0069]** If necessary, various additives such as a dissolution aid, a viscosity modifier, a pH adjusting agent, an antioxidant, a preservative, an antifungal agent, an anti-corrosion agent, and a chelating agent for capturing metal ions that give influence on dispersion may be appropriately added to the ink composition.

#### Imprinting Method

**[0070]** The imprinting method according to the embodiment includes a pre-treatment liquid adhering step of adhering a pre-treatment liquid of the textile printing ink set to a fabric, and a recording step of discharging the aqueous ink jet ink composition of the textile printing ink set from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.

#### Pre-Treatment Liquid Adhering Step

**[0071]** The pre-treatment liquid adhering step is a step of adhering the pre-treatment liquid of the textile printing ink set to the fabric. Means for adhering the pre-treatment liquid is not particularly limited, but, for example, roller coating, spray coating, and ink jet coating can be used.

### Recording Step

**[0072]** The recording step is a step of discharging the aqueous ink jet ink composition of the textile printing ink set from the head and adhering the aqueous ink jet ink composition to at least a portion of the adhesion area of the pre-treatment liquid on the fabric.

**[0073]** After the pre-treatment liquid adhering step, in a state in which 30% by mass or more of a volatile component of the pre-treatment liquid adhered to the fabric remains, the recording step is preferably performed. That is, in the imprinting method according to the embodiment, heating, ventilating, and leaving steps performed in order to dry the pre-treatment liquid can be omitted. Therefore, steps from the pre-treatment liquid adhering step to the recording step are performed in line, a drying step may not be provided therebetween, and thus the simplification of the device and the improvement of the productivity are achieved. If the general ink composition is used, as long as the pre-treatment liquid remains, the adhesiveness of the flocculating resin tends to decrease. However, according to the imprinting method according to the embodiment in which the ink set is used, even if the recording step is performed in a state in which 30% by mass or more of a volatile component of the pre-treatment liquid remains, the decrease of the adhesiveness can be suppressed. The remaining rate of the volatile component of the pre-treatment liquid is a ratio of an amount (mass) remaining on the fabric when the recording step is performed, with respect to adhesion amounts (mass) of the volatile component included in the pre-treatment liquid adhered to the fabric. The volatile component amount of the pre-treatment liquid can be measured by the method described in the example. The volatile component does not remain on the fabric after the pre-treatment liquid is dried, and water, an organic solvent, and the like are included.

### Heating Step

**[0074]** The imprinting method according to the embodiment preferably further includes a heating step of heating the fabric after the recording step. If the heating step is performed, a resin (polymer) included in the pre-treatment liquid or the ink composition can be fused on the surface of the fabric, and moisture can be evaporated. In addition, if the heating step is performed, the obtainable image tends to be excellent in the friction resistant.

**[0075]** In the heating step, the aqueous ink jet ink composition adhered surface on the fabric may not be subjected to a pressurizing process, or the aqueous ink jet ink composition adhered surface on the fabric may not be subjected to a pressurizing process, but it is preferable that the pressurizing process is not performed on the aqueous ink jet ink composition adhered surface on the fabric. As a heating method in which the aqueous ink jet ink composition adhered surface on the fabric is not subjected to the pressurizing process, oven drying (a method in which pressing is not performed such as conveyor oven and batch oven) is included. If the heating step is included, the productivity of the recorded matter is more improved. In addition, since the adhesiveness and the friction resistant are improved, the invention is particularly effective. In addition, the heating method in which the pressurizing process of the aqueous ink jet ink composition adhered surface is also performed on the fabric is not particularly limited, but, for example, heat press and wet-on-dry are included. In

addition, the expression “pressurizing” refers to applying the pressure by bringing an individual body into contact with the recording medium.

**[0076]** In addition, the heat source of the heating is not particularly limited, and, for example, an infrared ray (lamp) is included. The temperature of the heating process is not particularly limited, as long as the resin (polymer) included in the ink composition is fused, and the moisture is evaporated. The temperature is preferably 150° C. or higher, and more preferably in the range of about 150° C. to 200° C. If the temperature at the time of the heating process is in the range described above, the friction resistant can be further obtained.

**[0077]** After the heating step, the fabric may be washed and dried. At this point, if necessary, a soaping process, that is, a process of washing unfixed pigments with heat, soap liquid, or the like, may be performed.

### EXAMPLES

**[0078]** Hereinafter, the invention is described in detail with reference to examples and comparative examples. The invention is not intended to be limited by the following examples.

#### Materials for Pre-Treatment Liquid

**[0079]** The main materials for the pre-treatment liquid used in the examples and the comparative examples are as follows.

#### Polyvalent Metal Salt

**[0080]** Calcium nitrate tetrahydrate (manufactured by Kanto Kagaku)

**[0081]** Organic acid

**[0082]** Acetic acid (manufactured by Kanto Kagaku)

**[0083]** Resin

**[0084]** Vinyblan 1245L (vinyl acetate/acryl, solid content: 40%, manufactured by Nissin Chemical Industry Co., Ltd.)

#### Surfactant

**[0085]** BYK-348 (silicone-based surfactant, manufactured by BYK Japan KK)

#### Adjustment of Pre-Treatment Liquid

**[0086]** The respective materials are mixed in the composition presented in Table 1 and sufficiently stirred, so as to obtain respective pre-treatment liquids P1 to P2. In addition, in the Table 1, the unit of numerical values is % by mass, and a total amount is 100.0% by mass.

TABLE 1

Pre-treatment liquid No.		P1	P2
Polyvalent metal salt	Calcium nitrate tetrahydrate	7.5	—
Organic acid	Acetic acid	—	4
Resin	Vinyblan 1245L	10	5
Silicon-based surfactant	BYK348	0.15	0.15
	Pure water	Residual quantity	Residual quantity
	Total	100	100

## Material for Ink Composition

[0087] The main materials for the ink composition used in the examples and the comparative examples are as follows.

## Coloring Material

[0088] Titanium dioxide slurry (Product name: NanoTek® Slurry, manufactured by C.I. KASEI CO., LTD., solid content of titanium dioxide: 20%, and average particle diameter 250 nm)

## Resin Fine Particles (A)

[0089] Takelac W6021 (manufactured by Mitsui Chemicals, Inc., anionic urethane resin emulsion, self-dispersion type, solid content concentration: 30%)

[0090] Permarin UA-150 (Product name manufactured by Sanyo Chemical Industries, Ltd., anionic urethane resin emulsion, self-emulsion type, solid content concentration: 30%)

## Resin Fine Particles (B)

[0091] NK Binder R-5HN (manufactured by Shin-Nakamura Chemical Co., Ltd., acryl/styrene-based emulsion, emulsifier dispersion type, solid content concentration: 42.5%)

[0092] Vinyblan 2650 (manufactured by Nissin Chemical Industry Co., Ltd., acryl resin emulsion, emulsifier dispersion type, solid content concentration: 40%)

## Solvent

[0093] 2-pyrrolidone

## Glycerin

[0094] Triethylene glycol

[0095] Triethylene glycol monomethyl ether

## Surfactant

[0096] BYK-348 (Silicone-based surfactant, manufactured by BYK Japan KK)

## Adjustment of Ink Composition

[0097] The respective materials are mixed in the components presented in Table 2 described below, are sufficiently stirred, filtrated with a metal filter having a hole diameter of 5 μm, and are subjected to the deaeration processing by decompression with a vacuum pump, so as to obtain respective ink compositions W1 to W10, and WH1 and WH2. In addition, in Table 2 described below, the unit of the numerical values is % by mass, and the total amount is 100.0% by mass.

TABLE 2

		Ink composition No.					
		W1	W2	W3	W4	W5	W6
Coloring material	Titanium dioxide slurry	40.0	40.0	40.0	40.0	40.0	40.0
Resin fine particles (A)	Takelac W6021	20.0	20.0			30.0	18.0
	Permarin UA-150			20.0	20.0		
Resin fine particles (B)	NK Binder R-5HN	13.0		13.0			
	Vinyblan 2650		15.0		15.0	9.0	22.0
Solvent	2-pyrrolidone	2.0	2.0	2.0	2.0	2.0	2.0
	Glycerin	10.0	10.0	10.0	10.0	10.0	10.0
	Triethylene glycol	1.0	1.0	1.0	1.0	1.0	1.0
	Triethylene glycol monobutyl ether	1.0	1.0	1.0	1.0	1.0	1.0
Surfactant	BYK-348	0.3	0.3	0.3	0.3	0.3	0.3
	Ion exchanged water	Residual amount	Residual amount	Residual amount	Residual amount	Residual amount	Residual amount
	Total	100.0	100.0	100.0	100.0	100.0	100.0
	Pigment concentration (%)	8.0	8.0	8.0	8.0	8.0	8.0
	Solid content concentration of Resin fine particles (A)	6.0	6.0	6.0	6.0	9.0	5.4
	Solid content concentration of Resin fine particles (B)	5.5	6.0	5.5	6.0	3.6	8.8
	Solid content concentration of Resin fine particles (A) and (B)	11.5	12.0	11.5	12.0	12.6	14.2
	Resin solid content ratio of Resin fine particles (A)/Resin fine particles (B)	1.1	1.0	1.1	1.0	2.5	0.6

  

		Ink composition No.				
		W7	W8	W9	WH1	WH2
Coloring material	Titanium dioxide slurry	40.0	40.0	35.0	40.0	40.0
Resin fine particles (A)	Takelac W6021	30.0	15.0	30.0	30.0	
	Permarin UA-150					
Resin fine particles (B)	NK Binder R-5HN			16.0		30.0
	Vinyblan 2650		5.0	22.0		
Solvent	2-pyrrolidone		2.0	2.0	2.0	2.0
	Glycerin		10.0	10.0	10.0	10.0
	Triethylene glycol		1.0	1.0	1.0	1.0



TABLE 2-continued

Surfactant	Triethylene glycol monobutyl ether BYK-348	1.0	1.0	1.0	1.0	1.0
	Ion exchanged water	Residual amount	Residual amount	Residual amount	Residual amount	Residual amount
	Total	100.0	100.0	100.0	100.0	100.0
	Pigment concentration (%)	8.0	8.0	7.0	8.0	8.0
	Solid content concentration of Resin fine particles (A)	9.0	4.5	9.0	9.0	9.0
	Solid content concentration of Resin fine particles (B)	2.0	8.8	6.8	0.0	12.8
	Solid content concentration of Resin fine particles (A) and (B)	11.0	13.3	15.8	9.0	12.8
	Resin solid content ratio of Resin fine particles (A)/Resin fine particles (B)	4.5	0.5	1.3	—	0.0

#### Determination Method of Flocculency

**[0098]** 15 cc of a pre-treatment liquid is introduced to a 30 cc glass bottle. Further, respective resin fine particles are dripped with pipettes. At the time of dropping, the resin fine particles are solidified and separated from the pre-treatment liquid, and products which float on the water surface or sink to the bottom of the bottle are used as the resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid. In addition, when the resin fine particles are dripped with the pipettes, products that do not react or distinctively separated but that are entirely dissolved or that are clouded and dispersed, even though the resin comes into contact with the pre-treatment liquid, are used as the resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid.

**[0099]** Products were checked by the method described above. Takelac W6021 and Permarin UA-150 corresponded to the resin fine particles (A), with respect to the pre-treatment liquids P1 to P2. In addition, NK Binder R-5HN and Vinyblan 2650 correspond to the resin fine particles (B), with respect to the pre-treatment liquids P1 to P2.

#### Viscosity Measuring Method

**[0100]** The viscosity of the ink composition was obtained by the measurement in conformity with JIS Z8809 by using a vibration-type viscometer.

Examples 1 to 12 and Comparative Examples 1 to 3

#### Imprinting Method

**[0101]** Spray coating is evenly performed with the pre-treatment liquids in a coating amount of 3 g for about an A4 size on a fabric (manufactured by Hanes Inc. heavyweight, cotton: 100%, black-dyed cloth). After the spray coating, a fabric is set to an ink jet printer (SC-F2000 manufactured by Seiko Epson Corp.) in which one nozzle array of a head was filled with the ink compositions in the respective examples, the ink compositions are discharged from the nozzles, and the ink composition was adhered to the adhesion area of the pre-treatment liquid. At this point, the recording resolution was 1440×1440 dpi, and the adhesion amount was 100 mg/inch<sup>2</sup>. Thereafter, the fabric to which the ink composition was adhered was dried in an oven for 1 minute at 170° C. so as to obtain a recorded matter.

**[0102]** In addition, the residual ratio of the volatile component of the pre-treatment liquid adhered to the fabric when the

ink composition is adhered was about 80% by mass. In addition, the residual ratio of the volatile component was calculated based on data obtained by measuring the temporal change of the quantity of the fabric to which the pre-treatment liquid was adhered in advance. Here, the residual ratio of the volatile component when the pre-treatment liquid was adhered was set to 100%, the residual ratio of the volatile component when the mass of the fabric did not change even if the time elapsed was set to 0%, data in which the elapsed time from the adhesion and the residual ratio of the volatile component were related to each other was created in advance, and the residual amount of the volatile component at the corresponding time from the time elapsed from the adhesion can be obtained.

**[0103]** However, in Example 11, instead of the oven, heat press was performed for one minute at 170° C. In addition, in Example 12, after the pre-treatment liquid was adhered, the fabric was heated and dried, the ink composition was adhered to the fabric when the residual amount of the volatile component was about 0% by heating and drying the fabric. Further, in Comparative Example 3, the ink composition was adhered to the fabric without using the pre-treatment liquid.

#### Color Developing Properties

**[0104]** L\* values of the imprinted product obtained by the imprinting method were measured by a colorimeter (Product name manufactured by “Gretag Macbeth Spectrolino”, manufactured by X-RITE, Incorporated), and the color developing properties were evaluated based on the obtained L\* values by the following evaluation standards.

#### Evaluation Standard

- [0105]** S: L\* value is 94 or greater.
- [0106]** A: L\* value is 90 or greater and less than 94.
- [0107]** B: L\* value is 85 or greater and less than 90.
- [0108]** C: L\* value is less than 85.

#### Adhesiveness

**[0109]** A friction fastness test of rubbing the imprinted surface of the imprinted product obtained by the imprinting method described above 150 times using a tester (a Gakushin-type friction fastness tester AB-301S manufactured by Sangyo Co., Ltd.) with a load of 200 g was performed. The imprinted surface after the friction fastness test was checked in a level of “Dry” in conformity with Japanese Industrial Standards (JIS) JIS L0849 for checking a state in which ink is peeled off, so as to evaluate the adhesiveness.

## Evaluation Standard

**[0110]** A: A friction fastness degree is Grade 3 or higher.

**[0111]** B: A friction fastness degree is Grade 2.

**[0112]** C: A friction fastness degree is Grade 1.

TABLE 3

	Examples												Comparative Examples		
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Ink composition No.	W1	W1	W2	W3	W4	W5	W6	W7	W8	W9	W7	W7	WH1	WH2	W1
Ink viscosity	A	A	A	A	A	A	A	A	A	B	A	A	A	A	A
Pre-treatment liquid No.	P1	P2	P1	P1	P1	P1	P1	P1	P1	P1	P1	P1	P1	P1	—
Color developing properties	S	A	A	S	A	S	A	S	B	S	S	S	A	C	C
Adhesiveness	A	A	A	A	A	A	A	B	A	A	A	A	C	B	A

**[0113]** If Example 2 was compared with Example 1, it was found that color developing properties was more improved when polyvalent metal salt was used. In addition, if Examples 3, 7, and 9 were compared with Examples 1, 4, 8, and 10, it was found that color developing properties were more improved when the content of the solid content of the resin fine particles (A) was greater than that of the solid content of the resin fine particles (B). In addition, if Example 11 was compared with Example 8, it was found that friction resistant became satisfactory when the heat press was performed, but it was found that the feeling was excellent when the heat press was not performed. Further, if Example 12 was compared with Example 8, the adhesiveness tends to be more improved as the residual ratio of the volatile component becomes closer to 0%. However, if the ink set according to the embodiment was used, sufficient adhesiveness was achieved, even if the residual rate of the volatile component increased. In addition, the expression “feeling is deteriorated” indicates that a recorded area of the fabric is smoother than an unrecorded area when the fabric is touched with the hand and thus the feeling is different. Also, the expression “feeling is excellent” indicates that the feeling is not different. If the feeling is excellent, it is preferable since there is no uncomfortable feeling, when the fabric is touched.

**[0114]** If Comparative Example 1 was compared with the examples, it was found that the adhesiveness decreased, when the resin fine particles (B) were not included. In addition, if Comparative Example 2 was compared with the examples, it was found that the color developing properties decreased, if the resin fine particles (A) were not included. Further, if Comparative Example 3 was compared with the examples, it was found that color developing properties decreased if the pre-treatment liquid was not used.

**[0115]** The entire disclosure of Japanese Patent Application No. 2014-177500, filed Sep. 1, 2014 is expressly incorporated by reference herein.

What is claimed is:

1. A textile printing ink set comprising:

a pre-treatment liquid that contains a flocculant; and  
an aqueous ink jet ink composition,

wherein the aqueous ink jet ink composition contains resin fine particles (A) that flocculate by being mixed with the pre-treatment liquid and resin fine particles (B) that do not flocculate by being mixed with the pre-treatment liquid.

2. The textile printing ink set according to claim 1, wherein the resin fine particles (B) include at least one of an emulsifier dispersion-type resin or a nonionic resin.

3. The textile printing ink set according to claim 1, wherein the resin fine particles (A) include a self-dispersion-type anionic resin.

4. The textile printing ink set according to claim 1, wherein the resin fine particles (A) include a self-dispersion-type urethane resin, and  
the resin fine particles (B) include an emulsifier dispersion-type acryl resin.

5. The textile printing ink set according to claim 1, wherein the resin fine particles (A) include an anionic urethane resin, and  
the resin fine particles (B) include a nonionic urethane resin.

6. The textile printing ink set according to claim 1, wherein the aqueous ink jet ink composition further contains a white pigment.

7. The textile printing ink set according to claim 1, wherein a total content of solid contents of the resin fine particles (A) and the resin fine particles (B) is in a range of 8.0% by mass to 20% by mass with respect to a total amount of the aqueous ink jet ink composition,  
a content of the solid content of the resin fine particles (A) is in a range of 5.0% by mass to 12% by mass, with respect to a total amount of the aqueous ink jet ink composition, and

a content of the solid content of the resin fine particles (B) is in a range of 3.0% by mass to 10% by mass with respect to a total amount of the aqueous ink jet ink composition.

8. The textile printing ink set according to claim 1, wherein a content of the solid content of the resin fine particles (A) is greater than that of the solid content of resin fine particles (B).

9. An imprinting method, comprising:

adhering a pre-treatment liquid contained in the textile printing ink set according to claim 1 to a fabric; and  
discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 1 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area.

- 10. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 2 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 2 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 11. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 3 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 3 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 12. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 4 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 4 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 13. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 5 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 5 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 14. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 6 to a fabric; and

- discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 6 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 15. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 7 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 7 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 16. An imprinting method, comprising:  
adhering a pre-treatment liquid contained in the textile printing ink set according to claim 8 to a fabric; and discharging an aqueous ink jet ink composition contained in the textile printing ink set according to claim 8 from a head and adhering the aqueous ink jet ink composition to at least a portion of an adhesion area of the pre-treatment liquid on the fabric.
- 17. The imprinting method according to claim 9, wherein after the adhering of the pre-treatment liquid, in a state in which 30% by mass or more of a volatile component of the pre-treatment liquid adhered to the fabric remains, the discharging and adhering of the aqueous ink jet ink composition is performed.
- 18. The imprinting method according to claim 9, further comprising:  
heating the fabric after the discharging and adhering of the aqueous ink jet ink composition,  
wherein, in the heating of the fabric, a surface of the fabric to which the aqueous ink jet ink composition is adhered is not pressurized.

\* \* \* \* \*