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(11) **EP 1 724 311 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
22.11.2006 Bulletin 2006/47

(51) Int Cl.:
C09D 11/00 (2006.01) D06P 1/00 (2006.01)

(21) Application number: **06010391.8**

(22) Date of filing: **19.05.2006**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**
Designated Extension States:
AL BA HR MK YU

(30) Priority: **19.05.2005 JP 2005147094**
07.07.2005 JP 2005198602

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(54) **Ink for fabric printing and method for producing printed material**

(57) An ink for fabric printing is provided which has high washing fastness and is excellent in feel, sweat absorbing properties, appearance, and the like on fabric, and a method for producing a printed material is also provided. The ink for fabric printing contains a pigment and a resin emulsion. The weight ratio between the pigment and the solid resin content of the resin emulsion is in the range of from 1 : 0.7 to 1 : 3.0. The resin emulsion

contains a resin having a glass transition point of -25°C or higher and 18°C or lower and an acid value of 4 or more and 54 or less. The method for producing printed material includes: a printing step of performing printing by adhering the ink for fabric printing to fabric; and a fixing step of fixing the ink for fabric printing adhered to the fabric in the printing step on the fabric by heating.

EP 1 724 311 A1

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to an ink for fabric printing which is employed for forming an ink image on fabric by, for example, ejecting the ink by means of an ink-jet method, and to a method for producing a printed material.

2. Description of the Related Art

[0002] As a method for forming an ink image on fabric, a printing method employing ink-jet recording has previously been known (see Japanese Patent Application Laid-Open No. H08-283636). In this printing method, an ink containing a pigment and a resin emulsion is first ejected onto fabric by means of an ink-jet method to form a predetermined image, and the printed fabric is then subjected to a heat treatment to fix the pigment onto the fabric.

[0003] Moreover, as another method for forming an image on fabric, a method has been known in which a resin layer is formed on the surface of fabric by applying a plastizol ink containing a resin such as vinyl chloride.

[0004] However, in the ink-jet recording method employing pigments, after the ink is fixed by heating, the pigment contained in the ink may exhibit insufficient adhesion to the fabric, depending on the properties of a resin emulsion which is responsible for adhesion. Therefore, as the fabric is repeatedly washed, the pigment falls off, thereby causing a problem of color fading.

[0005] Further, in the method in which a plastizol ink containing a resin such as vinyl chloride is applied, a screen plate must be prepared since a screen printing method is employed. Also in this case, a thick resin layer formed on the surface of the fabric causes problems such as a stiff feeling and the degradation of sweat absorbing properties. Further, the plasticity of the resin layer decreases over time, causing problems such as the deterioration of the appearance due to the cracks of the resin layer.

SUMMARY OF THE INVENTION

[0006] The present invention has been made in view of the above. Accordingly, it is an object of the present invention to provide an ink for fabric printing which has high washing fastness and is excellent in feel, sweat absorbing properties, appearance, and the like on fabric as well as to provide a method for producing a printed material.

[0007] The above object has been achieved by the present invention to be described hereinafter. Accordingly, the present invention provides an ink for fabric printing comprising a pigment and a resin emulsion. The ink for fabric printing is configured such that a weight ratio between the pigment and a solid resin content of the resin emulsion is in a range of from 1 : 0.7 to 1 : 3.0, and that the resin emulsion contains a resin having a glass transition point of -25°C or higher and 18°C or lower and an acid value of 4 or more and 54 or less.

[0008] The present invention also provides a method for producing a printed material. This method comprises: a printing step of performing printing by adhering the abovementioned ink for fabric printing to fabric; and a fixing step of fixing the ink for fabric printing adhered to the fabric in the printing step on the fabric by heating.

[0009] The ink for fabric printing of the present invention contains a pigment and a resin emulsion in a specific ratio and the resin emulsion contains a resin having a specific glass transition point and a specific acid value. Therefore, this ink exhibits high density on a printed material and high washing fastness. In addition, excellent ejectability from a head and excellent intermittent ejectability are also achieved.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] The present invention relates to an ink for fabric printing comprising a pigment and a resin emulsion. Here, the weight ratio between the pigment and the solid resin content of the resin emulsion is in the range from 1 : 0.7 to 1 : 3.0. In addition, the resin emulsion contains a resin having a glass transition point of -25°C or higher and 18°C or lower and an acid value of 4 or more and 54 or less.

[0011] In the ink for fabric printing of the present invention, the weight ratio of the solid resin content of the resin emulsion to the pigment is 0.7 or more, and preferably 1.0 or more. Therefore, a printed material has high density, and high washing fastness is also obtained. When the ink for fabric printing of the present invention is employed, the ink is printed on fabric and is heated and fixed with an iron or the like. In this manner, the pigment firmly adheres to the fabric through the resin emulsion, and thus the density is not likely to decrease even after the fabric is washed.

[0012] Further, in the ink for fabric printing of the present invention, the weight ratio of the solid resin content of the resin emulsion to the pigment is 1 : 3.0 or less. Therefore, when printing is performed by use of, for example, an ink-jet

printer, high ejectability from a head and high intermittent ejectability are achieved. Specifically, the ink can be smoothly ejected from each of the nozzles of an ink-jet head during printing (ejectability from the head is high). In addition, even if the printing is suspended for a predetermined period of time and resumed thereafter, no nozzles which do not eject the ink are formed in the ink-jet head (the intermittent ejectability is high).

[0013] Moreover, when the ink for fabric printing of the present invention adheres to fabric, a thick resin layer is not formed on the surface of the fabric, unlike the case in which a plastizol ink containing a resin such as vinyl chloride is employed. Therefore, the fabric does not provide a stiff feeling, and sweat absorbing properties are not deteriorated. In addition, the appearance is not deteriorated due to the cracks of the resin layer.

[0014] Further, in the ink for fabric printing of the present invention, the resin emulsion contains a resin having a glass transition point of -25°C or higher and 18°C or lower and an acid value of 4 or more and 54 or less. Here, the glass transition point can be determined by a differential scanning calorimeter, and the acid value is equivalent to the amount (mg) of potassium hydroxide required to neutralize free fatty acids contained in 1 g of the resin.

[0015] In accordance with the present invention, since the glass transition point of the resin constituting the resin emulsion is -25°C or higher and 18°C or lower, tackiness and a stiff feeling (stiffness) after fixing are balanced with the adhesion to fibers. Further, since the acid value is 4 or more and 54 or less, both the stability of the emulsion in the ink and the washing fastness can be satisfied simultaneously.

[0016] Examples of the abovementioned resin emulsion include acrylic-based resin emulsions, vinyl acetate-based resin emulsions, urethane-based resin emulsions, polyester-based resin emulsions, silicone-based resin emulsions, olefin-based resin emulsions, and the like. Accordingly, examples of the resin constituting the resin emulsion include acrylic-based resins, vinyl acetate-based resins, urethane-based resins, polyester-based resins, olefin-based resins, and the like.

[0017] Examples of the pigment include black pigments (carbon black) such as C.I. Pigment Black 7, yellow pigments (monoazo yellow) such as C.I. Pigment Yellow 74, cyan pigments (phthalocyanine blue) such as C.I. Pigment Blue 15: 3, magenta pigments (quinacridone red) such as C.I. Pigment Red 122, and the like.

[0018] Examples of the fabric include cotton, polyester, cotton-polyester blends, and the like.

[0019] In the ink for fabric printing of the present invention, other components such as a pigment dispersing agent, a water-soluble organic solvent, a surfactant, a pH adjuster, and the like may be added.

[0020] Examples of the pigment dispersing agent include acrylic acid copolymers. The addition amount of the pigment dispersing agent may be, for example, 0.2 to 8 wt. %.

[0021] The water-soluble organic solvent may have the effect of adjusting viscosity and preventing water evaporation, and examples thereof include glycerin, ethylene glycol, diethylene glycol, propylene glycol, and the like. The addition amount of the water-soluble organic solvent may be, for example, 10 to 60 wt. %.

[0022] The surfactant may have the effect of adjusting the surface tension of the ink for fabric printing, and preferred examples thereof include acetylene glycol, alkylphenol ethylene oxide adducts, alkylbenzene sulfonates, sorbitan fatty acid esters, and the like. The addition amount of the surfactant may be, for example, 0.01 to 5 wt. %.

[0023] The pH adjuster may have the effect of finely adjusting and maintaining the pH, and preferred examples thereof include triethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane, sodium carbonate, and the like. The addition amount of the pH modifier may be, for example, 0.01 to 5 wt. %.

[0024] In the present invention, any resin emulsion produced by a known emulsion production method may be employed as the abovementioned resin emulsion. Preferably, a resin emulsion is employed which contains the resin emulsion particles formed in liquid. For example, a resin emulsion formed by an emulsion polymerization method is preferably employed.

[0025] If the resin emulsion particles contained in the ink for fabric printing of the present invention are formed in liquid, the particles have a spherical shape or a rounded shape. In this case, for example, the ink for fabric printing of the present invention produces the effect of enabling stable ejection from an ink-jet head even when the solid concentration of the resin emulsion increases.

[0026] Therefore, in the ink for fabric printing of the present invention, it is preferable that the particles of the resin emulsion be spherical. As used herein, the term "spherical" refers to that the ratio between the maximum diameter and the minimum diameter of the spherical particles, as measured by, for example, a scanning electron microscope (SEM), is in the range of from 1 : 0.7 to 1 : 1.

[0027] Examples of the method for forming the resin emulsion particles in liquid include emulsion polymerization, suspension polymerization, a method in which a solution containing a resin component dissolved therein is added dropwise to water at a fast rate to form the resin emulsion particles, and the like.

[0028] The ink for fabric printing of the present invention may be preferably applied to a method for producing a printed material by printing the ink on fabric. Specifically, the method for producing a printed material comprises: a printing step of performing printing by adhering the ink for fabric printing of the present invention to fabric; and a fixing step of fixing the ink for fabric printing adhered to the fabric in the printing step on the fabric by heating. This method for producing a printed material is also encompassed by the present invention.

[0029] In the method for producing a printed material according to the present invention, the ink for fabric printing of the present invention is employed to perform the printing step. Therefore, printing with high washing fastness can be performed. In addition, high ejectability from a head and high intermittent ejectability are achieved when an ink-jet printer is employed in the printing step.

[0030] Moreover, in the method for producing printed material of the present invention, the fixing step is provided. Therefore, the adhesion of the pigment and the resin emulsion to fabric is enhanced to thereby further improve the washing fastness.

[0031] Further, in the method for producing printed material according to the present invention, since a plastizol ink containing a resin such as vinyl chloride is not required, a thick resin layer is not formed on the surface of fabric. Therefore, the fabric does not provide a stiff feeling, and sweat absorbing properties are not deteriorated. In addition, the appearance is not deteriorated due to the cracks of the resin layer.

[0032] In the above-mentioned printing step, the ink for fabric printing can be made to adhere to fabric by use of, for example, an ink-jet head or a fabric conveying apparatus or the like.

[0033] In the above-mentioned fixing step, the heating can be performed with, for example, an iron. A suitable temperature for the heating is, for example, 150°C or higher. The heating temperature is set such that the pigment and the resin emulsion can be sufficiently fixed to fabric, but the fabric is not damaged. Further, a suitable heating time is 30 seconds or longer.

EXAMPLES

[0034] Embodiments (Examples) of the ink for fabric printing of the present invention will be described below.

Example 1

[0035] (a) The method for producing the ink for fabric printing will be described.

[0036] The components listed below were mixed in the after-mentioned ratios. The obtained mixtures were subjected to dispersion and mixing by means of a sand mill and a stirring apparatus to thereby produce inks for fabric printing of Examples 1-1 to 1-8. Table 1 shows the carbon black concentration (A), the resin emulsion concentration (solid content basis) (B), and the ratio B/A for the inks for fabric printing of Examples 1-1 to 1-8 and Comparative Examples 1-1 to 1-9 to be described below.

[0037] The resin emulsions contained in the inks for fabric printing of Examples 1-1 to 1-8 were produced by means of an emulsion polymerization method, and the emulsion particles thereof were spherical. In the inks for fabric printing, the balance (the component other than the components listed below) was pure water.

Table 1

		Pigment concentration (A) (wt.%)	Emulsion concentration (B) (wt.%)	B/A	Ejectability from head	Intermittent ejectability	OD value		Visual comparison before and after washing
							Before washing	After washing	
Example	1-1	8	6	0.75	A	A	1.15	1.00	A
	1-2	8	7	0.88	A	A	1.20	1.05	A
	1-3	8	8	1.00	A	A	1.20	1.10	AA
	1-4	8	9	1.13	A	A	1.20	1.10	AA
	1-5	8	10	1.25	A	A	1.20	1.10	AA
	1-6	8	16	2.00	A	A	1.25	1.20	AA
	1-7	8	20	2.50	A	A	1.25	1.25	AA
	1-8	8	24	3.00	A	A	1.25	1.25	AA
Comparative Example	1-1	5	0	0	A	A	0.80	0.40	B
	1-2	6	0	0	A	A	0.85	0.40	B
	1-3	7	0	0	A	A	0.90	0.40	B
	1-4	8	0	0	A	A	1.00	0.50	B
	1-5	8	5	0.63	A	A	1.10	0.90	B
	1-6	8	25	3.13	A	B	1.30	1.25	AA
	1-7	8	26	3.25	A	B	1.30	1.25	AA
	1-8	8	27	3.38	B	B	1.00	1.00	AA
	1-9	8	28	3.50	B	B	0.90	0.90	AA

(Example 1-1)

[0038]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt. %
 Acrylic resin emulsion: 6 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH adjuster): 0.1 wt. %

(Example 1-2)

[0039]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt. %
 Acrylic resin emulsion: 7 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH adjuster): 0.1 wt. %

(Example 1-3)

[0040]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt. %
 Acrylic resin emulsion: 8 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH adjuster): 0.1 wt. %

(Example 1-4)

[0041]

5 Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 9 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 10 Triethanolamine (pH adjuster): 0.1 wt.%

(Example 1-5)

[0042]

15 Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 10 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 20 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Example 1-6)

[0043]

25 Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 16 wt.% (solid content basis)
 30 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Example 1-7)

[0044]

35 Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 40 Acrylic resin emulsion: 20 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Example 1-8)

[0045]

45 Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 24 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

55 In addition, as Comparative Examples, the components listed below were mixed in the after-mentioned ratios. The obtained mixtures were subjected to dispersion and mixing by means of a sand mill and a stirring apparatus to thereby produce inks for fabric printing of Comparative Examples 1-1 to 1-9. The resin emulsions contained in these inks for fabric printing were produced by means of an emulsion polymerization method, and the emulsion particles

thereof were spherical. In the inks for fabric printing, the balance (the component other than the components listed below) was pure water.

(Comparative Example 1-1)

[0046]

Carbon black (C. I. Pigment Black 7, pigment): 5 wt.%
Acrylic acid copolymer (pigment dispersing agent): 1.0 wt.%
Diethylene glycol (water-soluble organic solvent): 20 wt.%
Acetylene glycol (surfactant): 0.1 wt.%
Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-2)

[0047]

Carbon black (C. I. Pigment Black 7, pigment): 6 wt.%
Acrylic acid copolymer (pigment dispersing agent): 1.2 wt.%
Diethylene glycol (water-soluble organic solvent): 20 wt.%
Acetylene glycol (surfactant): 0.1 wt.%
Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-3)

[0048]

Carbon black (C. I. Pigment Black 7, pigment): 7 wt.%
Acrylic acid copolymer (pigment dispersing agent): 1.4 wt.%
Diethylene glycol (water-soluble organic solvent): 20 wt.%
Acetylene glycol (surfactant): 0.1 wt.%
Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-4)

[0049]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
Diethylene glycol (water-soluble organic solvent): 20 wt.%
Acetylene glycol (surfactant): 0.1 wt.%
Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-5)

[0050]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
Acrylic resin emulsion: 5 wt.% (solid content basis)
Diethylene glycol (water-soluble organic solvent): 20 wt.%
Acetylene glycol (surfactant): 0.1 wt.%
Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-6)

[0051]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 25 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-7)

[0052]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 26 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-8)

[0053]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion: 27 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Comparative Example 1-9)

[0054]

Carbon black (C. I. Pigment Black 7, pigment): 8 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 1.6 wt.%
 Acrylic resin emulsion; 28 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

[0055] In Comparative Examples 1-1 to 1-5, the ratio of the amount of the resin emulsion to the amount of the pigment is less than 0.7 and thus is outside the scope of the present invention. Further, in Comparative Examples 1-6 to 1-9, the ratio of the amount of the resin emulsion to the amount of the pigment exceeds 3.0 and thus is outside the scope of the present invention.

[0056] (b) Next, the method for producing a printed material will be described which employs the inks for fabric printing of Example 1 to perform printing.

[0057] The printing was performed on fabric of 100% cotton at 50 pL x 600 dpi by use of an IJ printer (product of Brother Industries, Ltd.) (the printing step).

[0058] Subsequently, the printed portion was heated with an iron at a temperature of 180°C for 40 seconds to thereby fix the ink on the fabric (the fixing step).

[0059] (c) Next, a description will be given of the effects produced by the inks for fabric printing of Example 1 and the method for producing printed material using these inks.

[0060] (c-i) The inks for fabric printing of Example 1 have high washing fastness since the weight ratio of the solid resin content of the resin emulsion to the pigment is 1 : 0.7 or more. Therefore, when the ink for fabric printing of this Example is employed to perform printing on fabric and is heated and fixed with an iron or the like, the density is not likely to decrease even after the fabric is washed since the adhesion of the pigment to the fabric is high. Further, the printed material exhibits a high density of 1.15 or more.

[0061] (c-ii) In the inks for fabric printing of Example 1, the weight ratio of the solid resin content of the resin emulsion

to the pigment is set to 1 : 3.0 or less. In this manner, high ejectability from a head and high intermittent ejectability are achieved when printing is performed by use of an ink-jet printer. Specifically, the ink can be smoothly ejected from each of the nozzles of an ink-jet head during printing (the ejectability from the head is high). In addition, even if the printing is suspended for a predetermined period of time and resumed thereafter, no nozzles which do not eject the ink are formed in the ink-jet head (the intermittent ejectability is high).

[0062] (c-iii) The inks for fabric printing of Example 1 do not form a thick resin layer on the surface of fabric, unlike a plastizol ink containing a resin such as vinyl chloride. Therefore, the fabric does not provide a stiff, feeling, and sweat absorbing properties are not deteriorated. In addition, deterioration of the appearance due to the cracks of the resin layer does not occur.

[0063] (d) Next, a description will be given of experiments performed for confirming the effects of the inks for fabric printing of Example 1 and the method for producing a printed material using these inks.

[0064] (d-i) Washing fastness test

[0065] The washing fastness test was performed by means of a method in accordance with AATCC135-1995IIIA. Specifically, using each of the inks for fabric printing of Examples 1-1 to 1-8 and Comparative Examples 1-1 to 1-9, printing was first performed on a fabric of 100% cotton as in (b) described above. Subsequently, the printed portion was measured for density (the density before washing) by means of a Macbeth densitometer.

[0066] Subsequently, the fabric was washed by means of a method in accordance with AATCC135-1995IIIA, and the density after washing was obtained by means of a method similar to that described above. The results are shown in Table 1 above. As shown in Table 1, when the inks for fabric printing of Examples 1-1 to 1-8 were employed, the density difference before and after washing was 0.15 or less, and the density of the printed material after washing was more than 1.0. Thus, the washing fastness was confirmed to be high. On the contrary, when the inks for fabric printing of Comparative Examples 1-1 to 1-5 were employed, the density difference before and after washing was 0.2 or more, and the density of the printed material after washing was less than 1.0. Thus, the washing fastness was found to be low.

[0067] (d-ii) Test of ejectability from a head

[0068] Each of the inks for fabric printing of Examples 1-1 to 1-8 and Comparative Examples 1-1 to 1-9 was employed to print an area corresponding to an area of 10 sheets of A4 paper. The type of the printer and the printing conditions employed upon printing were the same as in (b) described above.

[0069] If no irregular printing was found in the printed area, a rank "A" was given for the evaluation of the ejectability from a head. If irregular printing was found, a rank "B" was given for the evaluation of the ejectability from a head. As used herein, the term "irregular printing" refers to that a nozzle which does not eject the ink is formed in the ink-jet head or to that the ink adheres to a portion to which the ink is not supposed to adhere. The evaluation results for the ejectability from a head are shown in Table 1 above.

[0070] As shown in Table 1, when the inks for fabric printing of Examples 1-1 to 1-8 were employed, the ejectability from a head was evaluated as "A" for all the inks. As can be seen from these results, the inks for fabric printing of Examples 1-1 to 1-8 exhibit excellent ejectability from a head. On the other hand, when the inks for fabric printing of Comparative Examples 1-8 and 1-9 were employed, the ejectability from a head was evaluated as "B."

[0071] (d-iii) Test of intermittent ejectability

[0072] Each of the inks for fabric printing of Examples 1-1 to 1-8 and Comparative Examples 1-1 to 1-9 was employed to print an area corresponding to an area of 10 sheets of A4 paper, and the printing was then suspended for 15 minutes. Subsequently, the printing was resumed, and an area corresponding to an area of a sheet of A4 paper was printed. The type of the printer and the printing conditions employed upon printing were the same as in (b) described above.

[0073] If no irregular printing was found in the paper printed after the 15 minute suspension, a rank "A" was given for the evaluation of the intermittent ejectability. If irregular printing was found, a rank "B" was given for the evaluation of the intermittent ejectability. The evaluation results for the intermittent ejectability are shown in Table 1 above. As shown in Table 1, when the inks for fabric printing of Examples 1-1 to 1-8 were employed, the intermittent ejectability was evaluated as "A" for all the inks. As can be seen from these results, the inks for fabric printing of Examples 1-1 to 1-8 exhibit excellent intermittent ejectability. On the other hand, when the inks for fabric printing of Comparative Examples 1-6 to 1-9 were employed, the intermittent ejectability was evaluated as "B."

[0074] (d-iv) Visual comparison test before and after washing

[0075] Before and after the washing in (d-i) above, the printed area was visually observed. The results are shown in Table 1 above. As shown, when the inks for fabric printing of Examples 1-1 to 1-8 were employed, no change was found in the appearance of the fabric before and after washing (evaluation: "AA"), or little change was found (evaluation: "A"). On the other hand, in Comparative Examples 1-1 to 1-5, the printed portion became fuzzy and whitish after washing (evaluation: "B").

Examples 1-3, 1-3a to 1-3g and Comparative Examples 1-3a to 1-3e

[0076] Among Examples 1-1 to 1-8, Example 1-3 was selected as a representative Example for evaluating the effects

of the glass transition point and the acid value of the resin constituting the resin emulsion on washing characteristics. Specifically, the same procedure as in Example 1-3 was repeated except that a resin emulsion shown in Table 2 was employed, thereby preparing the inks for fabric printing of Examples 1-3a to 1-3g and Comparative Examples 1-3a to 1-3e. The prepared inks were evaluated for "OD values before and after washing" and "visual comparison before and after washing," as in Example 1-3. The obtained results are shown in Table 2. Here, the glass transition point can be determined by a differential scanning calorimeter, and the acid value is equivalent to the amount (mg) of potassium hydroxide required to neutralize free fatty acids contained in 1 g of the solid resin content of the resin emulsion.

[0077] Each of the inks for fabric printing of Examples 1-3a to 1-3g and Comparative Examples 1-3a to 1-3e employs an acrylic resin of the same type as in Example 1-3 as the resin constituting the acrylic resin emulsion. Also, the compositions of the inks and the preparation methods of the inks are the same as in Example 1-3, except that the acrylic resin is used which has the glass transition points and the acid values recited in Table 2. Therefore, each of the above inks has a pigment concentration (A) of 8 wt.%, a resin emulsion concentration (a solid resin content) (B) of 8 wt. %, and a ratio (B) / (A) of 1.00.

Table 2

		Glass transition point (°C)	Acid value (mg KOH)	OD value		Visual comparison before and after washing
				Before washing	After washing	
Example	1-3	-25	4	1.20	1.10	AA
	1-3a	-5	54	1.15	1.10	AA
	1-3b	-4	44	1.15	1.05	AA
	1-3c	0	8	1.30	1.20	AA
	1-3d	9	13	1.30	1.20	AA
	1-3e	9	54	1.25	1.10	A
	1-3f	16	51	1.30	1.25	AA
	1-3g	18	13	1.15	1.00	A
Comparative Example	1-3a	0	100	1.20	1.00	B
	1-3b	12	87	0.90	0.55	B
	1-3c	16	100	1.15	0.95	B
	1-3d	22	> 60	1.15	0.70	B
	1-3e	50	7	1.20	1.00	B

[0078] As can be seen in Table 2, when the inks having a glass transition point of the resin emulsion of -25°C to 18°C and an acid value of 4 to 54 were employed, excellent OD values before and after washing and excellent visual comparison evaluation results before and after washing were obtained. On the contrary, if either of the glass transition point and the acid value was outside the abovementioned range, the obtained evaluation results were not satisfactory.

Example 2

[0079] (a) The components listed below were mixed in the after-mentioned ratios. The obtained mixtures were subjected to dispersion and mixing by means of a sand mill and a stirring apparatus to thereby produce inks for fabric printing of Examples 2-1 to 2-8. Table 3 shows the pigment concentration (A), the resin emulsion concentration (B), and the ratio B/A for the inks for fabric printing of Examples 2-1 to 2-8 and Comparative Examples 2-1 to 2-9 to be described below.

[0080] The resin emulsions contained in the inks for fabric printing of Examples 2-1 to 2-8 were produced by means of an emulsion polymerization method, and the emulsion particles thereof were spherical. In the inks for fabric printing, the balance (the component other than the components listed below) was pure water.

Table 3

		Pigment concentration (A) (wt.%)	Emulsion concentration (B) (wt.%)	B/A	Ejectability from head	Intermittent ejectability	OD value		Visual comparison before and after washing
							Before washing	After washing	
Example	2-1	3	2.1	0.70	A	A	0.97	0.90	A
	2-2	3	2.4	0.80	A	A	0.98	0.94	A
	2-3	3	2.7	0.90	A	A	1.00	0.94	AA
	2-4	3	3	1.00	A	A	1.00	0.95	AA
	2-5	3	3.3	1.10	A	A	1.00	0.95	AA
	2-6	3	6	2.00	A	A	1.05	1.05	AA
	2-7	3	7.5	2.50	A	A	1.05	1.05	AA
	2-8	3	9	3.00	A	A	1.10	1.10	AA
Comparative Example	2-1	1	0	0	A	A	0.54	0.30	B
	2-2	1.5	0	0	A	A	0.70	0.30	B
	2-3	2	0	0	A	A	0.76	0.40	B
	2-4	2.5	0	0	A	A	0.80	0.50	B
	2-5	3	1.5	0.50	A	A	0.90	0.70	B
	2-6	3	10	3.33	A	B	1.10	1.10	AA
	2-7	3	15	5.00	A	B	1.10	1.10	AA
	2-8	3	20	6.67	B	B	1.00	1.00	AA
	2-9	3	25	8.33	B	B	0.90	0.90	AA

(Example 2-1)

[0081]

Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 2.1 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH adjuster): 0.1 wt.%

(Example 2-2)

[0082]

Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 2.4 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-3)

[0083]

Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 2.7 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-4)

[0084]

5 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 3 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 10 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-5)

[0085]

15 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 3.3 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 20 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-6)

[0086]

25 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 Urethane resin emulsion: 6 wt.% (solid content basis)
 30 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-7)

[0087]

35 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 40 Urethane resin emulsion: 7.5 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier): 0.1 wt.%

(Example 2-8)

[0088]

45 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt.%
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt.%
 50 Urethane resin emulsion: 9 wt.% (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt.%
 Acetylene glycol (surfactant): 0.1 wt.%
 Triethanolamine (pH modifier) : 0.1 wt.%
 55

[0089] As Comparative Examples, the components listed below were mixed in the respective ratios. The obtained mixtures were subjected to dispersion and mixing by means of a sand mill and a stirring apparatus to thereby produce inks for fabric printing of Comparative Examples 2-1 to 2-9.

(Comparative Example 2-1)

[0090]

5 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 1, wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.2 wt. %
Diethylene glycol (water-soluble organic solvent): 20 wt. %
Acetylene glycol (surfactant): 0.1 wt. %
Triethanolamine (pH modifier): 0.1 wt. %

10

(Comparative Example 2-2)

[0091]

15 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 1.5 wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.3 wt. %
Diethylene glycol (water-soluble organic solvent): 20 wt. %
Acetylene glycol (surfactant): 0.1 wt. %
Triethanolamine (pH modifier): 0.1 wt. %

20

(Comparative Example 2-3)

[0092]

25 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 2 wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.4 wt. %
Diethylene glycol (water-soluble organic solvent): 20 wt. %
Acetylene glycol (surfactant): 0.1 wt. %
Triethanolamine (pH modifier): 0.1 wt. %

30

(Comparative Example 2-4)

[0093]

35 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 2.5 wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.5 wt. %
Diethylene glycol (water-soluble organic solvent): 20 wt. %
Acetylene glycol (surfactant): 0.1 wt. %
Triethanolamine (pH modifier): 0.1 wt. %

40

(Comparative Example 2-5)

[0094]

45 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.6 wt. %
Urethane resin emulsion: 1.5 wt. % (solid content basis)
Diethylene glycol (water-soluble organic solvent): 20 wt. %
Acetylene glycol (surfactant): 0.1 wt. %
50 Triethanolamine (pH modifier): 0.1 wt. %

(Comparative Example 2-6)

[0095]

55 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt. %
Acrylic acid copolymer (pigment dispersing agent): 0.6 wt. %
Urethane resin emulsion: 10 wt. % (solid content basis)

Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH modifier): 0.1 wt. %

5 (Comparative Example 2-7)

[0096]

10 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt. %
 Urethane resin emulsion: 15 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH modifier): 0.1 wt. %

15

(Comparative Example 2-8)

[0097]

20 Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt. %
 Urethane resin emulsion: 20 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH modifier): 0.1 wt. %

25

(Comparative Example 2-9)

[0098]

30

Monoazo yellow (C. I. Pigment Yellow 74, pigment): 3 wt. %
 Acrylic acid copolymer (pigment dispersing agent): 0.6 wt. %
 Urethane resin emulsion: 25 wt. % (solid content basis)
 Diethylene glycol (water-soluble organic solvent): 20 wt. %
 Acetylene glycol (surfactant): 0.1 wt. %
 Triethanolamine (pH modifier): 0.1 wt. %

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[0099] In Comparative Examples 2-1 to 2-5, the ratio of the amount of the resin emulsion to the amount of the pigment is less than 0.7 and thus is outside the scope of the present invention. Further, in Comparative Examples 2-6 to 2-9, the ratio of the amount of the resin emulsion to the amount of the pigment exceeds 3.0 and thus is outside the scope of the present invention.

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[0100] (b) Next, printing was performed on fabric by use of the inks for fabric printing of Example 2 and by means of the method for producing printed material same as that in Example 1.

[0101] (c) The same effects as in Example 1 are produced in the inks for fabric printing of Example 2 and the method for producing printed material using these inks.

45

[0102] (d) Next, in order to confirm the effects of the inks for fabric printing of Example 2 and the method for producing printed material using these inks, the tests of washing fastness, ejectability from a head, intermittence ejectability, and the appearance before and after washing were performed as in (d) of Example 1. The results are shown in Table 3.

[0103] (d-i) Washing fastness test

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[0104] As shown in Table 3, when the inks for fabric printing of Examples 2-1 to 2-8 were employed, the density difference before and after washing was 0.07 or less, and the density of the printed material after washing was 0.9 or more. Thus, the washing fastness was confirmed to be high. On the other hand, when the inks for fabric printing of Comparative Examples 2-1 to 2-5 were employed, the density difference before and after washing was 0.2 or more, and the density of the printed material after washing was 0.7 or less. Thus, the washing fastness was found to be low.

55

[0105] (d-ii) Test of ejectability from a head

[0106] As shown in Table 3, when the inks for fabric printing of Examples 2-1 to 2-8 were employed, the ejectability from a head was evaluated as "A" for all the inks. As can be seen from these results, the inks for fabric printing of Examples 2-1 to 2-8 exhibit excellent ejectability from a head. On the other hand, when the inks for fabric printing of

Comparative Examples 2-8 and 2-9 were employed, the ejectability from a head was evaluated as "B."

[0107] (d-iii) Test of intermittence ejectability

[0108] As shown in Table 3, when the inks for fabric printing of Examples 2-1 to 2-8 were employed, the intermittent ejectability was evaluated as "A" for all the inks. As can be seen from these results, the inks for fabric printing of Examples 2-1 to 2-8 exhibit excellent intermittent ejectability. On the other hand, when the inks for fabric printing of Comparative Examples 2-6 to 2-9 were employed, the intermittent ejectability was evaluated as "B."

[0109] (d-iv) Visual comparison test before and after washing

[0110] As shown in Table 3, when the inks for fabric printing of Examples 2-1 to 2-8 were employed, no change was found in the appearance of the fabric before and after washing (evaluation: "AA"), or little change was found (evaluation: "A"). On the other hand, in Comparative Examples 2-1 to 2-5, the printed portion became fuzzy and whitish after washing (evaluation: "B").

[0111] Further, for the inks for fabric printing of Examples 2-1 to 2-8, the preferable glass transition point and the preferable acid value of the employed resin emulsion are the same as those of Example 1-3 and 1-3a to 1-3g.

Example 3

[0112] Inks for fabric printing 3-1 to 3-8 were produced as in the inks for fabric printing of Examples 2-1 to 2-8, respectively, except that the kind of the pigment was changed to phthalocyanine blue (C. I. Pigment Blue 15:3). The same tests as those of (d) in Example 1 were performed by use of the inks for fabric printing 3-1 to 3-8, and similar results as in the inks for fabric printing of Examples 2-1 to 2-8 above were obtained. Also for the Example, the preferable glass transition point and the preferable acid value of the employed resin emulsion are the same as those of Example 1-3 and 1-3a to 1-3g.

Example 4

[0113] Inks for fabric printing 4-1 to 4-8 were produced as in the inks for fabric printing of Examples 2-1 to 2-8, respectively, except that the kind of the pigment was changed to quinacridone red (C. I. Pigment Red 122). The same tests as those of (d) in Example 1 were performed by use of the inks for fabric printing 4-1 to 4-8, and similar results as in the inks for fabric printing of Examples 2-1 to 2-8 above were obtained. Also for this Example, the preferable glass transition point and the preferable acid value of the employed resin emulsion are the same as those of Example 1-3 and 1-3a to 1-3g.

[0114] The present invention is not necessarily limited to the abovementioned Examples, and it is needless to say that the present invention can be embodied in various forms without departing from the scope of the present invention.

Claims

1. An ink for fabric printing comprising a pigment and a resin emulsion, wherein:

a weight ratio between the pigment and a solid resin content of the resin emulsion is in a range of from 1 : 0.7 to 1 : 3.0; and
the resin emulsion contains a resin having a glass transition point of -25°C or higher and 18°C or lower and an acid value of 4 or more and 54 or less.

2. The ink according to claim 1, wherein the weight ratio between the pigment and the solid resin content of the resin emulsion is in a range of from 1 : 1.0 to 1 : 3.0.

3. The ink according to claim 1 or 2, wherein particles contained in the resin emulsion are formed in liquid.

4. The ink according to claim 3, wherein the resin emulsion is formed by an emulsion polymerization.

5. The ink according to claim 3 or 4, wherein the particles have a spherical shape.

6. The ink according to any one of claims 3 to 5, wherein the ratio between the maximum diameter and the minimum diameter of the particles is in the range of 1 : 0.7 to 1 : 1.

7. The ink according to any one of claims 1 to 6, wherein the resin emulsion is an acrylic-based resin emulsion, vinyl acetate-based resin emulsion, urethane-based resin emulsion, polyester-based resin emulsion, silicone-based resin

emulsion, or olefin-based resin emulsion.

8. The ink according to any one of claims 1 to 7, wherein the pigment is carbon black, monoazo yellow, phthalocyanine blue, or quinacridone red.

9. The ink according to any one of claims 1 to 8, further comprising a pigment dispersing agent in an amount of 0.2 to 8 wt%.

10. The ink according to claim 9, wherein the pigment dispersing agent is an acrylic acid copolymer.

11. The ink according to any one of claims 1 to 10, further comprising a water-soluble organic solvent in an amount of from 10 to 60 wt%.

12. The ink according to claim 11, wherein the water-soluble organic solvent is selected from the group consisting of glycerin, ethylene glycol, diethylene glycol and propylene glycol.

13. The ink according to any one of claims 1 to 12, further comprising a surfactant in an amount of from 0.01 to 5 wt%.

14. The ink according to claim 13, wherein the surfactant is selected from the group consisting of acetylene glycol, alkylphenol ethylene oxide adducts, alkylbenzene sulfonates and sorbitan fatty acid esters.

15. The ink according to any one of claims 1 to 14, further comprising a pH regulator in an amount of from 0.01 to 5 wt%.

16. The ink according to claim 15, wherein the pH regulator is selected from the group consisting of triethanolamine, diethanolamine, tris(hydroxymethyl)aminomethane and sodium carbonate.

17. A method for producing a printed material, comprising:

a printing step of performing printing by adhering the ink according to any one of claims 1 to 16 onto fabric; and
a fixing step of fixing the ink adhered to the fabric in the printing step on the fabric by heating.

18. The method according to claim 17, wherein the ink is adhered onto the fabric by an ink-jet method.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 06 01 0391

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Place of search Munich		Date of completion of the search 21 June 2006	Examiner olde Scheper, B
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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