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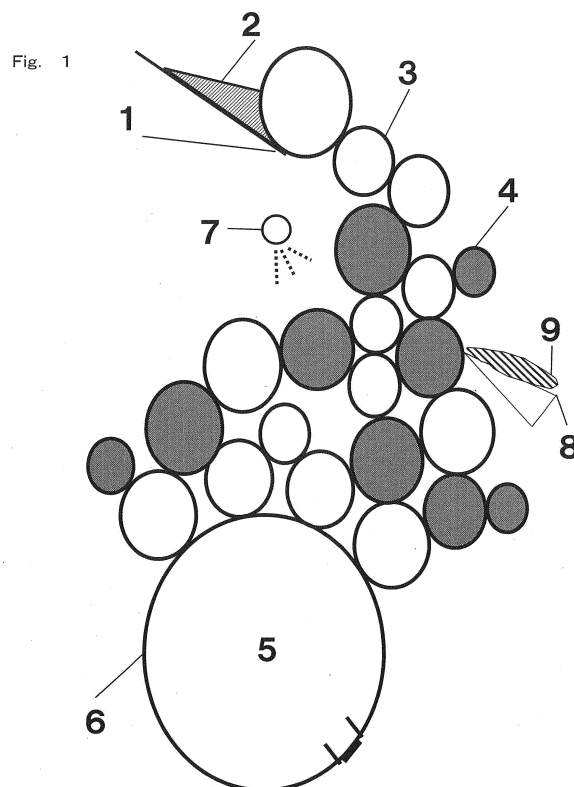
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(54) **DETERGENT FOR PRINTING MACHINES**

(57) The present invention provides a detergent for printing machines, said detergent containing at least water and a compound that contains an amino group and a carboxyl group, and having a pH of 8.0 to 13.0, inclusive. With this detergent for printing machines, it is easy to remove ink from the rollers of printing machines and efficiently clean the rollers. The present invention makes it possible to obtain a detergent for printing machines which generates minimal amounts of volatile organic compounds (VOC). This detergent for printing machines is safe and causes minimal environmental pollution. The present invention also provides a method for cleaning active energy beam-curable ink using a detergent for printing machines, said detergent containing at least water and a compound that contains an amino group and a carboxyl group, and having a pH of 8.0 to 13.0, inclusive. This method for cleaning active energy beam-curable ink facilitates installation to printing equipment, is safe, and causes minimal environmental pollution.



Description

Technical Field

5 **[0001]** The present invention relates to a detergent for printing machine. Furthermore, the present invention relates to a method for cleaning off an active energy ray-curable ink.

Background Art

10 **[0002]** In recent years, in order to prevent deterioration of the environment, and to improve the working environment, efforts to greatly reduce the use of volatile petroleum solvents in various printing fields, and to reduce the emission of volatile organic compounds (hereinafter referred to as "VOCs") are in progress. Since a large amount of petroleum solvents are used in general inks for printing machine, water-based inks or solvent-free inks have been asked for. Among others, an active energy ray-curable ink, which can be instantly cured by irradiation with ultraviolet rays or other active energy rays, has been expanding its use in many fields, because installment of the printing equipment is easy, and it is safe and less polluting to the environment, and highly productive. Patent Literature 1 discloses a composition of a detergent for offset printing, which is mainly composed of a glycol solvent, and capable of cleaning off an active energy ray-curable ink. Further, Patent Literature 2 discloses a detergent for printing machine water based ink that can be used for gravure and flexographic printing. However, the detergents presented in Patent Literature 1 and 2 contain a solvent which is carcinogenic or inflammable, and are highly volatile, and may deteriorate the global environment, and working environment, as well as safety and health. Therefore they need to be improved.

Citation List

25 Patent Literature

[0003]

30 Patent Literature 1: JP 2017-94663 A
Patent Literature 2: JP 2003-301197 A

Summary of Invention

Technical Problem

35 **[0004]** An object of the present invention is to provide a detergent for printing machine that is superior in washability and emits little VOC.
[0005] Furthermore, an object of the present invention is to provide a method for cleaning off an active energy ray-curable ink, which is implemented safely and causes little environmental pollution.

Solution to Problem

40 **[0006]** In order to achieve the above object, a detergent for printing machine of the present invention is a detergent for printing machine which comprises at least water and a compound having an amino group and a carboxyl group, and has a pH of 8.0 and more and 13.0 or less.
[0007] Further, the present invention is a method for cleaning off an active energy ray-curable ink using the detergent for printing machine which comprises at least water and a compound having an amino group and a carboxyl group, and has a pH of 8.0 and more and 13.0 or less.

Advantageous Effects of Invention

50 **[0008]** The detergent for printing machine of the present invention can easily remove an ink easily removed from the rollers of a printing machine, and can efficiently clean the rollers. According to the present invention a detergent for printing machine that emits little VOC (volatile organic compound) can be obtained. The detergent for printing machine of the present invention is safe and causes little environmental pollution.
[0009] According to the method for cleaning off an active energy ray-curable ink of the present invention, it is easy to install the printing equipment, is safe and causes little environmental pollution.

Brief Description of Drawings

[0010] Fig. 1 is a cross-sectional view of a device for testing the washability of an ink according to the present invention.

Description of Embodiments

[0011] The invention will be described in detail below.

[0012] The present invention is a detergent for printing machine which comprises at least water and a compound having an amino group and a carboxyl group, and has a pH of 8.0 or more and 13.0 or less.

[0013] The pH of the detergent for printing machine of the present invention is 8.0 or more, and preferably 10.0 or more. When the pH is 8.0 or more, the detergency is strong. The pH of the detergent for printing machine of the present invention is 13.0 or less, and preferably 12.0 or less. When the pH is 13.0 or less, the handling is easy.

[0014] As the compound having an amino group and a carboxyl group included in the detergent for printing machine of the present invention is preferably an amphoteric surfactant, or a commonly used amino acid.

[0015] Examples of the amphoteric surfactant include lauryl aminopropionate, lauryl dimethyl betaine, stearyl dimethyl betaine, lauryl dihydroxyethyl betaine, and 2-alkyl-*N*-carboxymethyl-*N*-hydroxyethylimidazolinium betaine. Among these, 2-alkyl-*N*-carboxymethyl-*N*-hydroxyethylimidazolinium betaine is particularly preferable, because it can alone raise the pH of the detergent to 8.0 or higher.

[0016] Examples of the amino acid include glycine, alanine, valine, leucine, isoleucine, methionine, proline, phenylalanine, tryptophan, serine, threonine, asparagine, glutamine, arginine, histidine, lysine, aspartic acid, glutamic acid, tyrosine, and cysteine. These amino acids may be either of L-isomer, or D-isomer, and a hydrochloride salt can also be used. These amino acids may be used singly or in a mixture of two or more kinds thereof. Since the pH of a detergent is regulated in a range of 8.0 to 13.0, a basic amino acid is preferable as the compound having an amino group and a carboxyl group. Basic amino acids include arginine, lysine, and histidine.

[0017] Since an amino acid has an amino group and a carboxyl group, it is highly soluble in water. Among the above, arginine is preferable, because it is easy to adjust the pH in a range of 8.0 to 13.0 by itself. A detergent containing arginine is particularly preferable, because it can be superior in washability and emits little VOCs. L-Arginine is especially preferable because it is easily available.

[0018] VOC (volatile organic compound) is defined according to U.S. EPA (Environmental Protection Agency) Method 24 as a compound that has a residual mass of less than 99% when heated at $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 1 hour, and includes a carbon atom in it. The weight loss rate excluding water of the detergent for printing machine of the present invention is preferably less than 1% when heated at 110°C at 1 atm for 1 hour, and more preferably less than 0.5%. The lower the weight loss rate is, the smaller the amount of VOC emission is. In such a case, a detergent for printing machine that has little impact on the human body and is superior in terms of the global environment, working environment, and safety and health can be obtained. As a device to be used for heating a detergent for printing machine, any publicly known conventional device may be used, and for example, an air-heating oven SPHH-200 (manufactured by TABAI MFG. CO., LTD.) may be used.

[0019] The VOC emission amount of a detergent for printing machine of the present invention can be measured by a photoionization detector (PID). The VOC emission amount of a detergent for printing machine of the present invention measured by a MiniRAE 3000 (produced by Honeywell International, Inc.) is preferably 100 ppm or less, more preferably 50 ppm or less, and most preferably 10 ppm or less.

[0020] The pH of a detergent for printing machine of the present invention may be adjusted in a range of pH 8.0 to 13.0 by using only a compound having an amino group and a carboxyl group, or in a range of pH 8.0 to 13.0 by using a combination of a compound having an amino group and a carboxyl group and an inorganic base. Further, the pH may be adjusted in a range of pH 8.0 to 13.0 by using a combination of a surfactant other than an amphoteric surfactant and an inorganic base.

[0021] According to the present invention, an inorganic base may be added for the purpose of adjusting the pH of a detergent for printing machine. The inorganic base is favorably used because it has a high boiling point and does not emit VOC. Specific examples of the inorganic base include an alkali metal carbonate, such as lithium carbonate, sodium carbonate, and potassium carbonate, an alkali metal bicarbonate, such as lithium hydrogencarbonate, sodium hydrogencarbonate, and potassium hydrogencarbonate, disodium hydrogenphosphate, lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, tetramethylammonium hydroxide, and tetraethylammonium hydroxide. These can be used singly or in combination of two or more kind thereof.

[0022] From the viewpoint of ensuring sufficient detergency, the content of the compound having an amino group and a carboxyl group is preferably 0.010 mass% or more with respect to the total amount of a detergent for printing machine as 100 mass%, and more preferably 1.0 mass% or more. From the viewpoint of the solubility of the compound having an amino group and a carboxyl group in water, the content of the compound having an amino group and a carboxyl group is preferably 20.0 mass% or less, more preferably 10.0 mass% or less, and further preferably 5.0 mass% or less.

[0023] In the detergent for printing machine of the present invention, an amino acid is preferably used as the compound having an amino group and a carboxyl group. From the viewpoint of ensuring sufficient detergency, the content of the amino acid is preferably 0.010 mass% or more with respect to the detergent for printing machine as 100 mass%, and more preferably 1.0 mass% or more. From the viewpoint of the solubility of the amino acid in water, the content of the amino acid is preferably 20.0 mass% or less, more preferably 10.0 mass% or less, and further preferably 5.0 mass% or less. The amino acid content is more preferably 0.010 mass% or more and 20.0 mass% or less.

[0024] The content of a compound having an amino group and a carboxyl group in a detergent for printing machine can be easily measured by GC-MS. By dissolving a sample in water to 1.0 mass% and subjecting the same to a GC-MS (EI, CI) measurement, the content of a compound having an amino group and a carboxyl group in a detergent for printing machine can be measured. The content of an amino acid can also be easily measured by GC-MS in the same way.

[0025] The detergent for printing machine according to the present invention may optionally contain an anionic surfactant or a cationic surfactant. The detergent for printing machine according to the present invention may also contain any surfactants other than an amphoteric surfactant. The detergent for printing machine according to the present invention may also contain a nonionic surfactant. When such a surfactant is contained, the wettability of the surfaces of a resin-made doctor blade is improved, so that the scraping property for the solution is favorably improved.

[0026] Examples of an anionic surfactant include a fatty acid salt, a hydroxyalkane sulfonate, an alkane sulfonate, a dialkylsulfosuccinate, a polyoxyethylene alkylsulfophenyl ether salt, a *N*-methyl-*N*-oleyltaurine sodium salt, a *N*-alkyl-sulfosuccinic acid monoamide disodium salt, a polyoxyethylene alkyl ether sulfate, a fatty acid monoglyceride sulfate, an alkyl phosphates, and a polyoxyethylene alkyl ether phosphate

[0027] Examples of a cationic type surfactant include an alkylamine salt, a quaternary ammonium salt, a polyoxyethylene alkylamine salt, and a polyethylene polyamine derivative.

[0028] Examples of a nonionic surfactant include a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene polystyrylphenyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a polyoxyethylene-polyoxypropylene block copolymer, a glycerol fatty acid partial ester, a sorbitan fatty acid partial ester, a pentaerythritol fatty acid partial ester, a propylene glycol monofatty acid ester, a sucrose fatty acid partial ester, a polyoxyethylene sorbitan fatty acid partial ester, a polyoxyethylene sorbitol fatty acid partial ester, a polyethylene glycol fatty acid ester, a polyglycerol fatty acid partial ester, a polyoxyethylated castor oil, a polyoxyethylene glycerol fatty acid partial ester, a fatty acid diethanolamide, a *N,N*-bis-2-hydroxyalkylamine, a polyoxyethylene alkylamine, a triethanolamine fatty acid ester, and a trialkylamine oxide.

[0029] A detergent containing a nonionic surfactant is preferable because it facilitates scraping of an ink with a doctor blade and emits only a small amount of VOCs. When a detergent contains polyoxyethylene sorbitan fatty acid partial ester among other nonionic surfactants, it is further preferable because it further facilitates scraping of an ink with a doctor blade, and emits less VOCs

[0030] The HLB (Hydrophilic-Lipophilic Balance) of the nonionic surfactant is preferably 10 or more from the viewpoint of solubility in water, more preferably 12 or more, and further preferably 13 or more. The HLB is preferably 20 or less from the viewpoint of ink solubility, more preferably 19 or less, and further preferably 18 or less. The HLB of the nonionic surfactant is still more preferably 10 or more and 20 or less. Here, the HLB indicates the molecular weight of the hydrophilic group portion of the entire molecular weight of the surfactant, and for a nonionic surfactant it is calculated according to the following Griffin's formula:

$$\text{HLB} = 20 \times \left(\frac{\text{molecular weight of hydrophilic group portion in surfactant}}{\text{molecule/molecular weight of surfactant}} \right)$$

[0031] The hydrophilic group portion of a nonionic surfactant in the detergent for printing machine of the present invention is preferably ethylene oxide groups from the viewpoint of facilitating removal of the remaining detergent with water after cleaning of an ink. Further, the nonionic surfactant preferably has an ethylene oxide group. Specific examples thereof include a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene polystyrylphenyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a polyoxyethylene polyoxypropylene block copolymer, a polyoxyethylene sorbitan fatty acid partial ester, a polyoxyethylene sorbitol fatty acid partial ester, a polyethylene glycol fatty acid ester, a polyoxyethylated castor oil, a polyoxyethylene glycerol fatty acid partial ester, and a polyoxyethylene alkylamine. Polyoxyethylene sorbitan monolaurate is most preferable, because it has high solubility in an ink, is rinsed excellently with water, and does not fall under the GHS described below.

[0032] The average number of moles of ethylene oxide group added is preferably 2 or more, more preferably 4 or more, and further preferably 5 or more. From the viewpoint of handling property and prevention of surfactant precipitation, the average number of moles of ethylene oxide group added is 50 or less, preferably 40 or less, and further preferably

30 or less,

[0033] The content of the nonionic surfactant is preferably 5 mass% or more, more preferably 10 mass% or more, and further preferably 15 mass% or more, from the viewpoint of facilitating scraping of an ink and a detergent for printing machine with a doctor blade. From the viewpoint of removing an ink with a small amount of detergent, it is preferably 40 mass% or less, more preferably 30 mass% or less, and further preferably 25 mass% or less. The content of the nonionic surfactant is more preferably 5 mass% or more and 40 mass% or less.

[0034] Since offset printing is normally performed in a range of 10°C to 30°C, it is preferable that the detergent for printing machine of the present invention is liquid in a range of 10°C to 30°C. The surfactant is preferably also liquid in a range of 10°C to 30°C because rinsing with water becomes easy.

[0035] The water content in the detergent for printing machine of the present invention is preferably 40 mass% or more, and more preferably 60 mass% or more, from the viewpoint of suppressing the emission amount of VOCs. From the viewpoint of ink solubility, it is preferable that the water content is 99.99 mass% or less. It is further preferable that the water content in the detergent for printing machine of the present invention is 40 mass% or more and 99.99 mass% or less.

[0036] The detergent for printing machine of the present invention may be used in an automatic roller cleaning device. The viscosity of the detergent for printing machine refers to the viscosity measured one minute after the start of stirring in accordance with JIS K7117-1:1999 using a Brookfield type B digital viscometer at a liquid temperature of 25°C. From the viewpoint of preventing dripping in using an automatic roller cleaning device, the viscosity of the detergent for printing machine is preferably 1.0 mPa·s or higher, and even more preferably 5.0 mPa·s or higher. From the viewpoint of facilitating cleaning with an automatic cleaning device, the viscosity of the detergent for printing machine is preferably 200 mPa·s or less, and more preferably 150 mPa·s or less. It is preferable that the viscosity of the detergent for printing machine at 25°C is from 1.0 mPa·s to 200 mPa·s.

[0037] It is preferable that raw materials to be used for the detergent for printing machine of the present invention are not controlled under the Globally Harmonized System of Classification and Labelling of Chemicals (hereinafter referred to as "GHS"). In this regard, it is provided that the GHS is an internationally harmonized system and rules for criteria to classify chemicals based on the types and degree of hazards, and the content for labels or safety data sheets. Since it is provided in the GHS that as communication tools pictograms that visually indicate the characteristics of hazards, and statements of recommended measures for handling, etc. are to be used, it is possible to determine whether a product is subject to the GHS from the descriptions thereof.

[0038] Chemicals subject to the GHS are labeled with a hazard category. In this regard, hazard category refers to the classification of criteria within each hazard class. Each category is indicated by a number, wherein a smaller number indicates a higher risk. The categories are classified according to the relative risks of the hazard within a hazard class.

[0039] The detergent for printing machine of the present invention can be used for cleaning off an ink adhered to various components of a printing machine, and it is particularly preferable to use it for cleaning off an air-blow drying ink or an active energy ray-curable ink.

[0040] In the cleaning method using the detergent for printing machine of the present invention, an ink that has been adhered to the plate, roller, blanket, impression cylinder, etc. during a flexographic or offset printing operation comes into contact with the detergent for printing machine, thereby performing a cleaning process. For example, an ink adhered during a flexographic or offset printing operation to the plate, the printing machine, or the like is wiped off with a piece of cloth directly impregnated with the detergent during a printing operation, or alternatively it may be used as a detergent dedicated to a plate cleaning device, an automatic roller cleaning device, an automatic blanket cleaning device, etc. The cleaning method using the detergent for printing machine of the present invention preferably further includes thereafter a cleaning step with water.

[0041] It is preferable that the detergent for printing machine of the present invention is used for cleaning off an active energy ray-curable ink. It is more preferable that the detergent for printing machine of the present invention is used for an active energy ray-curable ink containing a polyfunctional (meth)acrylate having a hydroxyl group. Since an active energy ray-curable ink has a high polarity, its solubility in the detergent according to the present invention is high, and as a result, excellent washability can be obtained.

[0042] Preferable specific examples of a polyfunctional (meth)acrylates having a hydroxyl group include a poly(meth)acrylate of a polyhydric alcohol, such as trimethylolpropane, glycerol, pentaerythritol, diglycerol, di(trimethylolpropane), and di(pentaerythritol), as well as alkylene oxide adducts of the above.

[0043] It is preferable that the detergent for printing machine of the present invention is applied to an active energy ray-curable ink containing a resin having a hydrophilic group. Since the ink is highly soluble in the detergent for printing machine of the present invention owing to its high polarity, excellent washability can be obtained.

[0044] Examples of the hydrophilic group of the resin having a hydrophilic group include a polyethylene oxide group, a hydroxyl group, a carboxyl group, a sulfo group, and a phosphate group. Among these, a carboxyl group, which gives superior dispersion of a pigment, is particularly preferable.

[0045] Specific examples of the resin having a hydrophilic group include, but not particularly limited to, an acrylic resin,

a styrene-acrylic resin, a styrene-maleic acid resin, a rosin-modified maleic acid resin, a rosin-modified acrylic resin, an epoxy resin, a polyester resin, a polyurethane resin, and a phenolic resin.

[0046] The acid value of the resin having a hydrophilic group is preferably 30 mg KOH/g or more and 250 mg KOH/g or less. In order to obtain excellent solubility of the resin in the detergent for printing machine, the acid value of the resin having a hydrophilic group is preferably 30 mg KOH/g or more, more preferably 60 mg KOH/g or more, and further preferably 75 mg KOH/g or more. It is even more desirable to have 75 mg KOH/g or higher. Further, from the viewpoint of handling property of an ink, it is preferably 250 mg KOH/g or less, more preferably 230 mg KOH/g or less, and further preferably 210 mg KOH/g or less. The acid value of a resin included in an active energy ray-curable ink is further preferably 30 mg KOH/g or more and 250 mg KOH/g or less.

[0047] The acid value of a resin having a hydrophilic group may be determined in accordance with the test method of "Section 3.1 Neutralization Titration Method" in JIS K 0070:1992 "Test methods for acid value, saponification value, ester value, iodine value, hydroxyl value and unsaponifiable matter of chemical products".

[0048] The detergent for printing machine is preferably a detergent for offset printing machine.

[0049] By the method for cleaning off an active energy ray-curable ink of the present invention, an active energy ray-curable ink is cleaned off by using a detergent for printing machine, which comprises at least water and a compound having an amino group and a carboxyl group, and has a pH of 8.0 or more and 13.0 or less. By the method for cleaning off an active energy ray-curable ink of the present invention, an active energy ray-curable ink is cleaned off preferably by using a detergent for printing machine, which comprises at least water and an amino acid, and has a pH of 8.0 or more and 13.0 or less. By the method for cleaning off an active energy ray-curable ink of the present invention, an active energy ray-curable ink is cleaned off more preferably by using a detergent for printing machine, which comprises at least water and a basic amino acid, and has a pH of 8.0 or more and 13.0 or less.

[0050] The method for cleaning off an active energy ray-curable ink of the present invention is more preferably performed for the cleaning time of 10 min or less. The measurement of a cleaning time starts when the doctor blade comes into contact with the roller and ends when it is visually recognized that the ink and the detergent for printing machine are completely removed.

[0051] For the roller cleaning in offset printing, cleaning is preferably performed such that the ink applied onto the roller is dissolved with a detergent, and the resulting detergent is scraped off with a resin-made doctor blade.

[0052] Since a doctor blade is expendable, a doctor blade made of a thermoplastic resin, which can be manufactured at low cost, is preferably used. Further, also from the viewpoint of not damaging the roller surface, a doctor blade made of a thermoplastic resin is preferable. Examples of the thermoplastic resin include polyethylene (PE), a polyester, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(ethylene naphthalate) (PEN), polypropylene (PP), polyamide (PA), polycarbonate (PC), polyetherimide (PEI), polyetheretherketone (PEEK), polyetherketone (PEK), polyethersulfone (PES), polyimide (PI), polyacetal (POM), poly(phenylene sulfide) (PPS), polystyrene (PS), and polyurethane (PU). Among these, at least one selected from the group consisting of polyethylene (PE), polyester, and polyacetal (POM) is preferably used from the viewpoint of wear resistance and adherence to the roller in the cross-machine direction.

[0053] From the viewpoint of superior scraping property with respect to an ink and a detergent for printing machine of the doctor blade, it is preferable that the contact angle of the doctor blade surface with respect to water is 50 degree or less. When the contact angle is 50 degree or less, the wettability of the ink detergent to the blade surface is enhanced, and the detergent can easily flow to the washing vat downstream of the blade. From the viewpoint of shortening the cleaning time, the contact angle of the doctor blade surface with respect to water is preferably 40 degree or less, and more preferably 20 degree or less. Examples of a method to reduce the contact angle with respect to water to 50 degree or less include a coating treatment with a hydrophilic resin, a UV irradiation treatment, a flame treatment, a corona discharge treatment, and a plasma treatment. From the viewpoint of attaining uniform surface treatment, a UV irradiation treatment, a corona discharge treatment, or a plasma treatment is preferable, and from the viewpoint of the durability of the surface treatment, a plasma treatment is more preferable.

[0054] In the present invention, the contact angle of the doctor blade surface with respect to water is the value measured by a static method using a doctor blade of the aforescribed material instead of the glass substrate described in JIS (Japanese Industrial Standards) R3257:1999 "Testing method of wettability of glass substrate" of the Japanese Industrial Standards. This value was measured using a doctor blade made of the materials listed above by the static method.

[0055] As a gas for a plasma treatment, any publicly known gases other than a fluorine gas may be used. As such a gas for a plasma treatment, that containing an oxygen gas may be favorably used. In that case, a hydrophilic group, such as a carboxyl group, a hydroxy group, and a carbonyl group, may be formed on the doctor blade surface. It is more preferable to perform a plasma treatment using only an oxygen gas. It is further preferable to form fine irregularities on the doctor blade surface using a gas, such as argon and helium, and then to perform a plasma treatment using an oxygen gas. In this way, a doctor blade highly hydrophilized may be obtained.

[0056] In the method for cleaning off an active energy ray-curable ink of the present invention, it is more preferable that the number of applications of the detergent in offset printing is 10 or less. In the evaluation of the washability in

offset printing, the presence or absence of an ink residue adhered to the ink roller was visually inspected. As a single application of a detergent for printing machine, 20 mL of a detergent listed in Table 1 was applied onto the ink roller, which was repeated at intervals of 1 min.

[0057] In the method for cleaning off an active energy ray-curable ink of the present invention, it is more preferable that the number of wipes required for washing off all ink in a washability evaluation in flexographic printing is two or less. In the washability evaluation in flexographic printing, the resin plate is wiped with waste cloth soaked with a detergent for printing machine described in Examples, and the presence or absence of an ink residue on the resin plate was visually inspected. The wiping from an end of the resin plate to the other end was counted as one wipe.

Examples

[0058] The present invention will be described in more detail by way of Examples below.

<Example of Production of Air-blow Drying Ink for Offset Printing>

<Resin Varnish I>

[0059]

Styrene-maleic acid resin: "ARASTAR" (registered trademark) 700 (produced by ARAKAWA HEMICAL INDUSTRIES, LTD.): 32 mass%
Solvent I: Propylene glycol (produced by Wako Pure Chemical Industries, Ltd.): 51.85 mass%
Solvent II: Glycerol (produced by Wako Pure Chemical Industries, Ltd.): 6 mass%.
Polyether polyamine I: diethanolamine (produced by Wako Pure Chemical Industries, Ltd.): 10 mass%.
Polyether polyamine II: "JEFFAMINE" (registered trademark) T403 (produced by Huntsman Corporation): 0.15 mass%

[0060] The styrene-maleic acid resin, polyether polyamine I, polyether polyamine II, solvent I, and solvent II weighed out in the above proportions were heated with stirring at 130°C for 2 hours to dissolve the styrene-maleic acid resin, and then cooled to room temperature to yield a resin varnish I.

<Ink I>

[0061]

Lionol Blue 7330 (produced by TOYO INK CO., LTD): 20 parts by mass
Resin varnish I: 75 parts by mass
Solvent I: Propylene glycol: 4 parts by mass
PE wax: 1 part by mass

[0062] The above materials were weighed out to form a mixture, which was kneaded through a three-roll mill "EXAKT" (registered trademark) M-80S (manufactured by EXAKT Technologies, Inc.) with a roller gap at scale 1 three times to yield an air-blow drying ink for offset printing.

<Example of Production of Active Energy Ray-curable Ink for Offset Printing>

<Resin Composition>

[0063] Resin I: One point four equivalent of glycidyl methacrylate (GMA) was added to cause a reaction with carboxyl groups of a copolymer composed of 25 mass% of methyl methacrylate, 25 mass% of styrene, and 50 mass% of methacrylic acid to yield resin I having ethylenic unsaturated groups and hydrophilic groups. The yielded resin I had a weight average molecular weight of 34,000, an acid value of 102 mg KOH/g, and an iodine value of 2.0 mol/kg.

<Resin Varnish II>

[0064]

	Resin I:	21.8 mass%
	Polyfunctional	(meth)acrylate I having a hydroxyl group "Miramer" (registered trademark) M340 (produced by Miwon Specialty Chemical Co., Ltd.): 64 mass%
5	Polyfunctional	(meth)acrylate II having a hydroxyl group "Miramer" (registered trademark) 4004 (produced by Miwon Specialty Chemical Co., Ltd.): 14 mass%
10	Polymerization inhibitor I:	p-methoxyphenol (produced by Wako Pure Chemical Industries, Ltd.): 0.2 mass%.

[0065] Weighing out the materials in the above proportions, the resin I and the polymerization inhibitor I were added to a mixed solvent of the polyfunctional (meth)acrylate I having a hydroxyl group and the polyfunctional (meth)acrylate II having a hydroxyl group heated to 90°C. The mixture was then stirred to dissolve the resin I and then cooled to room temperature to yield the resin varnish II.

<Ink II>

[0066]

	Seika	Cyanine Blue (produced by Dainichiseika Color & Chemicals Mfg. Co., Ltd.): 20 mass%.
	Resin I:	12 mass%
	Polyfunctional (meth) acrylate I	having a hydroxyl group: 24 mass%
25	Polyfunctional (meth) acrylate II	having a hydroxyl group: 33 mass%
	Photoinitiator I:	"IRGACURE" (registered trademark) 907 (produced by BASF): 5 mass%
	Sensitizer I:	Diethylaminobenzophenone (produced by TOKYO CHEMICAL INDUSTRY CO., LTD.): 5 mass%.
30	Polymerization inhibitor I:	p-methoxyphenol (Wako Pure Chemical Industries, Ltd.): 1 mass%.

[0067] The above materials were weighed out to form a mixture, which was kneaded through a three-roll mill "EXAKT" (registered trademark) M-80S (manufactured by EXAKT Technologies, Inc.) with a roller gap at scale 1 three times to yield an active energy ray-curable ink for offset printing.

<Doctor Blade>

- [0068]** Polyethylene (ultra-high molecular weight polyethylene, new light (white) doctor blade, produced by Saxin Corp.)
[0069] Polyester doctor blade ("Plastic Doctor" (registered trademark), Hi-PET, manufactured by Fuji Shoko Co., Ltd.)
[0070] Polyacetal doctor blade ("Plastic Doctor" (registered trademark), Hi-POM manufactured by Fuji Shoko Co., Ltd.)

<Hydrophilization Treatment of Doctor Blade>.

[0071] The doctor blade was subjected to a hydrophilization treatment by a plasma treatment under the following conditions.

1. Gas species: Oxygen
2. Gas flow rate: 1000 sccm
3. Pressure: 20 Pa
4. Applied high-frequency power: 1500 W (frequency 13.56 MHz)
5. Treatment time: 2 min

<Measurement of Contact Angle of Doctor Blade Surface with Respect to Water>

[0072] To measure the contact angle of the doctor blade surface with respect to water, 3 μ L of pure water at 25°C

and as an instrument DMO-501 manufactured by Kyowa Interface Science Co., Ltd. were used. The contact angle was measured 30 sec after the pure water came into contact with the doctor blade surface.

<Measurement of pH>

[0073] The pH was measured using a pH meter F-52 (manufactured by Horiba Co., Ltd.) at a liquid temperature of 25°C in accordance with JIS Z 8802:2011.

[0074] <Washability Test>

<Flexographic Printing>

[0075] A photosensitive resin plate ("TORELIEF" (registered trademark) DWF95DIII, manufactured by Toray Industries, Inc.) was mounted on a flexographic printing test machine (Flexiproof 100, manufactured by RK Print Coat Instruments Ltd.), in which the line number of the anilox roll was 400. The ink I was supplied to print 500 copies on PET (polyethylene terephthalate) sheets ("NOVACLEAR" (registered trademark), thickness: 100 μm, manufactured by Mitsubishi Chemical Corporation). Afterwards, the cylinder was wiped with waste cloth soaked with a detergent for printing machine described in Example, and the washability was visually rated.

<Offset Printing>

[0076] A waterless offset printing plate (TAN-E, manufactured by Toray Industries, Inc.) was mounted on an offset printing machine (OLIVER 266EPZ, manufactured by Sakurai Graphic Systems Corporation). The ink I or the ink II was supplied such that the reflectance density in the solid print area became 1.6 (indigo), and 500 copies were printed. After that, 20 mL of the detergent described in Example was applied onto the roller at intervals of 1 min, and a doctor blade (NEWLIGHT Doctor Blade manufactured by Shinoda & Co. Ltd., thickness: 27 mm) was used to remove the dissolved ink and the detergent for printing machine.

[0077] Fig. 1 shows a cross-sectional view of a device used according to the present invention for testing the washability of an ink. An ink is placed in the ink pot. The ink is transferred by rollers to a printing plate on the printing cylinder. After the ink is used for printing, the rest is recovered by a doctor blade.

[0078] The measurement of a cleaning time started when the doctor blade came into contact with the roller and ended when it was visually recognized that the ink and the detergent for printing machine were completely removed. The cleaning time is preferably 10 min or less, and more preferably 5 min or less. A detergent which required a cleaning time of 20 min or more was rated that it was not capable of cleaning.

<Evaluation of Washability: Flexographic Printing>

[0079] The washability was rated according to the following criteria.

- A: All the ink was washed off by wiping once.
- B: All the ink was washed off by wiping twice.
- C: An ink residue remained even after wiping three or more times.

[0080] In the washability evaluation in flexographic printing, the resin plate is wiped with waste cloth soaked with a detergent for printing machine described in Examples, and the presence or absence of an ink residue on the resin plate was visually inspected. The wiping from an end of the resin plate to the other end was counted as one wipe.

<Evaluation of Washability: Offset Printing>

[0081] The washability was rated according to the following criteria.

- A: The ink could be removed by applying a detergent 5 times or less.
- B: The ink could be removed by applying a detergent 6 times or more but 10 times or less.
- C: The ink could be removed by applying a detergent 11 times or more but 15 times or less.
- D: An ink residue remained even after applying a detergent 16 times or more.

[0082] In the evaluation of the washability in offset printing, the presence or absence of an ink residue adhered to the ink roller was visually inspected. As a single application of a detergent for printing machine, 20 mL of a detergent listed in Table 1 was applied onto the ink roller, which was repeated at intervals of 1 min.

<Measurement of VOC Emission Amount>

[0083] The emission amount of VOCs was measured by placing a MiniRAE 3000 (manufactured by Honeywell International, Inc.) at 30 cm above the roller when the washability test was performed.

<Measurement of Viscosity>

[0084] A viscosity was measured using a B type digital viscometer DV-E (manufactured by Brookfield Engineering Co., Ltd.) at a liquid temperature of 25°C one minute after the start of stirring in accordance with JISK7117-1:1999.

<Evaluation According to Method 24>

[0085] The raw materials to be included in a detergent for printing machine other than water were weighed out in a predetermined ratio to prepare a mixture, 3 g of which was weighed and placed in an aluminum cup. The sample was heated in an air-heating oven SPHH-200 (manufactured by TABAI MFG. CO., LTD.) at 110°C for 1 hour, and then the heating residue rate (weight after heating / weight before heating) was measured. In a case in which the heating residue rate was 99% or more, it was judged that the detergent for printing machine was not a VOC.

<With or Without GHS Mark>

[0086] The SDS of each raw material was referred for existence of a GHS mark. The SDS is an acronym for Safety Data Sheet, which is a document listing hazard information on a chemical substance, and provided from a business operator when the chemical substance or a product containing the chemical substance is transferred or supplied to another business operator. A raw material without a GHS mark was judged to be superior in terms of impact on the human body, global environment, or work environment, and safety and health.

<Ingredients of Detergent>

(Basic Compound)

Ethanolamine

Triethanolamine

(Amino Acid)

[0087]

L-histidine (produced by KYOWA HAKKO BIO CO., LTD.)

Glycine (produced by KYOWA HAKKO BIO CO., LTD.)

L-proline (produced by KYOWA HAKKO BIO CO., LTD.)

L-alanine (produced by KYOWA HAKKO BIO CO., LTD.)

L-methionine (produced by KYOWA HAKKO BIO CO., LTD.)

L-tyrosine (produced by KYOWA HAKKO BIO CO., LTD.)

L-arginine (produced by KYOWA HAKKO BIO CO., LTD.)

(Inorganic Base)

[0088] Potassium hydroxide (produced by Wako Pure Chemical Industries, Ltd.)

(Nonionic Surfactant)

[0089] Any of the following nonionic surfactants are liquid in a range of 10°C to 30°C. The numbers in parentheses represent the average number of moles of ethylene oxide group added.

Polyoxyethylene(5) lauryl ether (produced by Kao Corporation)

Polyoxyethylene(9) lauryl ether (produced by Kao Corporation)

Polyoxyethylene(4) oleyl ether (produced by Kao Corporation)

Polyoxyethylene(9) oleyl ether (produced by Kao Corporation)
 Polyoxyethylene(5) alkyl(sec-C11-15) ether (produced by Kao Corporation)
 Polyoxyethylene(9) alkyl(sec-C11-15) ether (produced by Kao Corporation)
 Polyoxyethylene(12) monolaurate (produced by Kao Corporation)
 Polyoxyethylene(10) monooleate (produced by Kao Corporation)
 Polyoxyethylene(30) sorbitol tetraolate (produced by Kao Corporation)
 Polyoxyethylene(6) sorbitan monolaurate (produced by Kao Corporation)
 Polyoxyethylene(20) sorbitan monopalmitate (produced by Kao Corporation)
 Polyoxyethylene(20) sorbitan monolaurate (produced by Kao Corporation).

(Example 1)

[0090] A detergent for printing machine was prepared by weighing out the detergent ingredients shown in Table 1 and stirring the mixture thereof for 10 min. The pH was measured to find that the pH of the obtained detergent for printing machine was 11.2. A washability test was performed by a flexographic printing method with AQUA CONTE K (produced by TOYO INK CO., LTD). The ink could be wiped off completely from the printing plate by wiping twice. The emission amount of VOC was measured to find 50 ppm. The SDS of each raw material was referred for a GHS mark to find the following marks for potassium hydroxide.

Skin corrosion and irritation: hazard category 2

Serious eye damage or eye irritation: hazard category 1

Specific target organ systemic toxicity (single exposure): hazard category 2 (respiratory system)

[0091] As a result of a measurement according to Method 24, the heating residue rate was 99.6 mass%, so it was judged that the detergent for printing machine in Example 1 was not a VOC. When the viscosity was measured, it was 2 mPa·s, so it was judged that the product could be used in an automatic roller cleaning device.

(Examples 2 and 3, and Comparative Example 1)

[0092] The respective detergents were evaluated in the same operations as in Example 1, except that each detergent composition was changed as set forth in Table 1. The results are shown in Table 1.

[Table 1]

	Composition of detergent				Viscosity (mPa·s)	pH (25°C)	Printing method	Washability (Flexo)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emis- sion amount (ppm)
	Water	pH adjuster										
	Content / (mass%)	Amino acid	Content / (mass%)	inorganic base	Content / (mass%)							
Example 1	98	L-Histidine	1.0	Potassium hydroxide	1.0	11.2	Flexo	B	99.6%	-	W/	50
Example 2	99	L-Histidine	1.0	-	-	8.5	Flexo	B	99.6%	-	W/O	50
Example 3	99	L-Arginine	1.0	-	-	11.0	Flexo	A	99.6%	-	W/O	50
Comparative Example 1	99	Glycine	1.0	-	-	6.6	Flexo	C	99.6%	Not washable	W/O	50

[0093] AQUA CONTE K was used as the ink.

(Example 4)

5 **[0094]** A detergent for printing machine was prepared by weighing out the detergent ingredients shown in Table 2 and stirring the mixture thereof for 10 min. The pH was measured to find that the pH of the obtained detergent for printing machine was 11.2. A washability test was performed by an offset printing method with the ink I. The ink could be removed completely from the roller within 10 min from the start of washing. The emission amount of VOC was measured to find 50 ppm. The SDS of each raw material was referred for a GHS mark to find the same marks as in Example 1 for potassium hydroxide.

10 **[0095]** As a result of a measurement according to Method 24, the heating residue rate was 99.6 mass%, so it was judged that the detergent for printing machine in Example 4 was not a VOC. When the viscosity was measured, it was 2 mPa·s, so it was judged that the product could be used in an automatic roller cleaning device.

15 (Examples 5 to 8, and Comparative Examples 2 and 3)

[0096] The respective detergents for printing machine were evaluated in the same operations as in Example 4, except that each detergent composition was changed as set forth in Table 2. The results are shown in Table 2.

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[Table 2]

	Composition of detergent										Viscosity (mPa-s)	HLB	pH (25 °C)	Print- ing meth- od	Blade			Washa- bility (Off- set)	Meth- od 24	Clean- ing time (min)	W/or W/O GHS mark	VOC emis- sion amount (ppm)
	Water	pH adjuster				Nonionic surfactant		Material	W/ or W/O plasma treat- ment	Con- tact an- gle												
		Amino acid (mass %)	Con- tent / (mass %)	inorgan- ic base	Con- tent / (mass %)	Name	Con- tent / (mass %)															
Example 4	98	L-Histi- dine	1.0	Potassi- um hy- droxide	1.0	-	-	2	-	11.2	Offset	Polyethyl- ene	W/O	90	B	99.6%	10	W/	50			
Example 5	99	L-Histi- dine	1.0	-	-	-	-	2	-	8.5	Offset	Polyethyl- ene	W/O	90	C	99.6%	15	W/O	50			
Example 6	99	L-Ar- ginine	1.0	-	-	-	-	2	-	11.0	Offset	Polyethyl- ene	W/O	90	B	99.6%	10	W/O	50			
Example 7	79	L-Ar- ginine	1.0	-	-	Polyoxyeth- ylene(6) sorbitan monolaurate	20	15	13.3	11.0	Offset	Polyethyl- ene	W/O	90	A	99.4%	5	W/O	50			
Example 8	79	L-Ar- ginine	1.0	-	-	Polyoxyeth- ylene(20) sorbitan monolaurate	20	15	16.7	11.0	Offset	Polyethyl- ene	W/O	90	A	99.6%	5	W/O	50			
Compara- tive Exam- ple 2	99	Glycine	1.0	-	-	-	-	2	-	6.6	Offset	Polyethyl- ene	W/O	90	D	99.6%	Not washa- ble	W/O	50			
Compara- tive Exam- ple 3	99	-	-	Potassi- um hy- droxide	1.0	-	-	2	-	11.2	Offset	Polyethyl- ene	W/O	90	D	99.6%	Not washa- ble	W/	50			

[0097] The ink I was used as the ink.

(Example 9)

5 **[0098]** A detergent for printing machine was prepared by weighing out the detergent ingredients shown in Table 3 and stirring the mixture thereof for 10 min. The pH was measured to find that the pH of the obtained detergent for printing machine was 11.2. A washability test was performed by an offset printing method with the ink II. The ink II could be removed completely from the roller within 8 min from the start of washing. The emission amount of VOC was measured to find that it was less than 10 ppm. The SDS of each raw material was referred for a GHS mark to find the same marks as in Example 1 for potassium hydroxide. As a result of a measurement according to Method 24, the heating residue rate was 99.6 mass%, so it was judged that the detergent for printing machine in Example 9 was not a VOC. When the viscosity was measured, it was 2 mPa·s, so it was judged that the product could be used in an automatic roller cleaning device.

15 (Examples 10 to 15, and Comparative Example 4)

[0099] The respective detergents were evaluated in the same operations as in Example 9, except that each detergent composition was changed as set forth in Table 3. The results are shown in Table 3.

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[Table 3]

	Composition of detergent					Viscosity (mPa·s)	pH (25 °C)	Blade			Washability (Offset)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emission amount (ppm)
	Water	pH adjuster			Material			W/ or W/O plasma treatment	Contact angle						
		Amino acid	Content / (mass %)	inorganic base						Content / (mass %)					
Example 9	98	L-Histidine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 10	98	Glycine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 11	98	L-Proline	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 12	98	L-Alanine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 13	98	L-Methionine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 14	98	L-Tyrosine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Example 15	98	2-Alkyl-N-car- boxymethyl-N- hydroxyethyl imidazolinium betaine	1.0	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	B	99.6%	8	W/	<10
Comparative Example 4	99	-	-	Potassium hydroxide	1.0	2	11.2	Polyethylene	W/O	90	D	99.6%	Not wash- able	W/	<10

[0100] The ink II was used as the ink.

(Examples 16 to 20, and Comparative Examples 5 to 7)

5 **[0101]** The respective detergents were evaluated in the same operations as in Example 9, except that each detergent composition was changed as set forth in Table 4. The results are shown in Table 4.

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[Table 4]

	Composition of detergent			Viscosity (mPa·s)	pH (25°C)	Blade			Washability (Offset)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emis- sion amount (ppm)
	Water	pH adjuster											
		Content / (mass%)	Amino acid			Content / (mass%)							
Example 16	99	L-Histidine	1.0	2	8.5	Polyethylene	W/O	90	C	99.6%	13	W/O	<10
Example 17	98	2-Alkyl-N-carboxyme- thyl-N-hy- droxyethyl- imidazolinu m betaine	1.0	2	10.0	Polyethylene	W/O	90	B	99.6%	9	W/O	<10
Example 18	99	L-Arginine	1.0	2	11.0	Polyethylene	W/O	90	B	99.6%	8	W/O	<10
Example 19	99.99	L-Arginine	0.01	2	10.0	Polyethylene	W/O	90	B	99.6%	9	W/O	<10
Example 20	80	L-Arginine	20.0	2	12.0	Polyethylene	W/O	90	B	99.6%	6	W/O	<10
Comparative Example 5	99	Glycine	1.0	2	6.6	Polyethylene	W/O	90	D	99.6%	Not washa- ble	W/O	<10
Comparative Example 6	99	Eth- anolamine	1.0	2	12.5	Polyethylene	W/O	90	B	0.0%	10	W/	200
Comparative Example 7	99	Trieth- anolamine	1.0	2	10.7	Polyethylene	W/O	90	C	0.0%	13	W/	200

[0102] The ink II was used as the ink.

(Examples 21 to 33)

5 **[0103]** The respective detergents were evaluated in the same operations as in Example 9, except that each detergent composition was changed as set forth in Table 5. The results are shown in Table 5.

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[Table 5]

	Composition of detergent						Viscosity (mPa-s)	HLB	pH (25 °C)	Blade			Washabili- ty (Offset)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emission amount (ppm)
	Water	pH adjuster	Nonionic surfactant		Content / (mass%)	Material				W/ or W/O plasma treatment	Contact angle						
			Content / (mass%)	Name													
Example 21	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(5) lauryl ether	20	50	10.5	11.0	Polyethylene	W/O	90	A	97.7%	3	W/	10	
Example 22	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(9) lauryl ether	20	15	13.6	11.0	Polyethylene	W/O	90	A	99.5%	3	W/	<10	
Example 23	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(4) oleyl ether	20	70	8.8	11.0	Polyethylene	W/O	90	A	99.8%	3	W/	<10	
Example 24	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(9) oleyl ether	20	30	12	11.0	Polyethylene	W/O	90	A	99.9%	3	W/	<10	
Example 25	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(5) alkyl (sec-C11-15) ether	20	30	10.5	11.0	Polyethylene	W/O	90	A	99.7%	3	W/	<10	
Example 26	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(9) alkyl (sec-C11-15) ether	20	15	13.3	11.0	Polyethylene	W/O	90	A	99.6%	3	W/	<10	
Example 27	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(12) monol- aurate	20	50	13.7	11.0	Polyethylene	W/O	90	A	99.9%	3	W/	<10	
Example 28	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(10) mo- nooleate	20	50	11.6	11.0	Polyethylene	W/O	90	A	99.9%	3	W/	<10	
Example 29	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(30) sorbitol tetraoelate	20	10	10.5	11.0	Polyethylene	W/O	90	A	100.0%	3	W/	<10	

(continued)

	Composition of detergent						Viscosity (mPa-s)	HLB	pH (25 °C)	Blade			Washabili- ty (Offset)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emission amount (ppm)
	Water	pH adjuster		Nonionic surfactant		Material				W/ or W/O plasma treatment	Contact angle						
		Content / (mass%)	Amino acid	Content / (mass%)	Name												
Example 30	79	L-Ar- ginine	1.0		Polyoxyethyl- ene(6) sorbitan monolaurate	20	50	13.3	11.0	Polyethylene	W/O	90	A	99.4%	3	W/O	<10
Example 31	89	L-Ar- ginine	1.0		Polyoxyethyl- ene(6) sorbitan monolaurate	10	15	13.3	11.0	Polyethylene	W/O	90	A	99.4%	4	W/O	<10
Example 32	94	L-Ar- ginine	1.0		Polyoxyethyl- ene(6) sorbitan monolaurate	5	10	13.3	11.0	Polyethylene	W/O	90	A	99.4%	4	W/O	<10
Example 33	49	L-Ar- ginine	1.0		Polyoxyethyl- ene(6) sorbitan monolaurate	50	100	13.3	11.0	Polyethylene	W/O	90	A	99.4%	5	W/O	<10

[0104] The ink II was used as the ink.

(Examples 34 to 38)

5 **[0105]** The respective detergents were evaluated in the same operations as in Example 9, except that each detergent composition was changed as set forth in Table 6. The results are shown in Table 6.

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[Table 6]

	Composition of detergent						Viscosity (mPa·s)	HLB	pH (25°C)	Blade			Washabili- ty (Offset)	Method 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emission amount (ppm)
	Water	pH adjuster	Nonionic surfactant		Material	W/orW/O plasma treatment				Contact angle							
			Content/ (mass%)	Name							Content/ (mass%)						
Example 34	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan mon- opalmitate	20		15	15.6	11.0	Polyethyl- ene	W/O	90	A	96.9%	3	W/O	<10
Example 35	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20		15	16.7	11.0	Polyethyl- ene	W/O	90	A	99.6%	3	W/O	<10
Example 36	89	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	10		10	16.7	11.0	Polyethyl- ene	W/O	90	A	99.6%	4	W/O	<10
Example 37	94	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	5		5	16.7	11.0	Polyethyl- ene	W/O	90	A	99.6%	4	W/O	<10
Example 38	49	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	50		100	16.7	11.0	Polyethyl- ene	W/O	90	A	99.6%	5	W/O	<10

[0106] The ink II was used as the ink.

(Example 39)

5 **[0107]** An ink washing test was conducted in the same manner as in Example 9, except that the doctor blade of Example 35 was changed to that made of a polyethylene ("Plastic Doctor" (registered trademark) Hi-PE) manufactured by Fuji Shoko Co., Ltd.) undergone a hydrophilization treatment under the conditions described in the section of <Hydrophilization treatment of doctor blade>. The results are shown in Table 7.

10 (Example 40)

[0108] An ink washing test was conducted in the same manner as in Example 9, except that the doctor blade of Example 35 was changed to that made of a polyester ("Plastic Doctor" (registered trademark) Hi-PET) manufactured by Fuji Shoko Co., Ltd.) undergone a hydrophilization treatment under the conditions described in the section of <Hydrophilization treatment of doctor blade>. The results are shown in Table 7.

(Example 41)

20 **[0109]** An ink washing test was conducted in the same manner as in Example 9, except that the doctor blade of Example 35 was changed to that made of a polyacetal ("Plastic Doctor" (registered trademark) Hi-POM) manufactured by Fuji Shoko Co., Ltd.) undergone a hydrophilization treatment under the conditions described in the section of <Hydrophilization treatment of doctor blade>. The results are shown in Table 7.

(Example 42)

25 **[0110]** A doctor blade was prepared by conducting a hydrophilization treatment on a polyacetal doctor blade ("Plastic Doctor" (registered trademark) Hi-POM) manufactured by Fuji Shoko Co., Ltd.) in which the gas species was changed from oxygen to argon. An ink washing test was conducted in the same manner as in Example 9 using this doctor blade. The results are shown in Table 7.

30 (Example 43)

[0111] A doctor blade was prepared by further conducting a hydrophilization treatment on the doctor blade having undergone the hydrophilization treatment in Example 38, in which the gas species was changed to oxygen. An ink washing test was conducted in the same manner as in Example 9 using this doctor blade. The results are shown in Table 7.

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[Table 7]

	Composition of detergent					Viscosity (mPa·s)	HLB	pH (25 °C)	Blade				Washabili- ty (Offset)	Metho d 24	Cleaning time (min)	W/ or W/O GHS mark	VOC emission amount (ppm)
	Water	pH adjuster	Nonionic surfactant		Material				W/ or W/O pla- sma treatment	Kind of gas	Contact angle						
	Content (mass %)	Amino acid	Content (mass %)	Name		Content (mass %)											
Example 39	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20	15	16.7	11.0	Polyethyl- ene	W/ 	Oxygen	35	A	99.6%	2	W/O	<10
Example 40	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20	15	16.7	11.0	Polyester	W/ 	Oxygen	30	A	99.6%	2	W/O	<10
Example 41	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20	15	16.7	11.0	Polyacetal	W/ 	Oxygen	15	A	99.6%	2	W/O	<10
Example 42	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20	15	16.7	11.0	Polyacetal	W/ 	Argon	45	A	99.6%	2	W/O	<10
Example 43	79	L-Ar- ginine	1.0	Polyoxyethyl- ene(20) sorb- itan monolau- rate	20	15	16.7	11.0	Polyacetal	W/ 	Argon Oxygen	10	A	99.6%	2	W/O	<10

[0112] The ink II was used as the ink.

[0113] As can be understood from the results in Tables 1 to 7, a detergent which contains a compound having an amino group and a carboxyl group, and has a pH of 8.0 or more and 13.0 or less exhibits excellent capability of cleaning in a short time and an effect of suppressing the emission amount of VOC.

Industrial Applicability

[0114] With the detergent for printing machine of the present invention, an ink can be easily removed from the rollers of a printing machine, and the rollers can be efficiently cleaned. According to the present invention a detergent for printing machine that emits little VOC (volatile organic compound) can be obtained. The detergent for printing machine of the present invention is safe and causes little environmental pollution.

[0115] According to the method for cleaning off an active energy ray-curable ink of the present invention, it is easy to install the printing equipment, is safe and causes little environmental pollution.

Reference Signs List

[0116]

1. ink pot
2. ink
3. ink oscillator roller (made of resin or rubber)
4. metal roller
5. printing cylinder
6. printing plate
7. application position of cleaning solution
8. doctor blade
9. recovered ink

Claims

1. A detergent for printing machine which comprises at least water and a compound having an amino group and a carboxyl group, and has a pH of 8.0 or more and 13.0 or less.
2. The detergent for printing machine according to claim 1, wherein the compound is an amino acid.
3. The detergent for printing machine according to claim 2 containing an amino acid at 0.010 mass% or more and 20.0 mass% or less.
4. The detergent for printing machine according to claim 2 or 3, wherein the amino acid is a basic amino acid.
5. The detergent for printing machine according to any one of claims 2 to 4, wherein the amino acid is arginine.
6. The detergent for printing machine according to any one of claims 1 to 5, wherein the viscosity of the detergent for printing machine at 25°C is from 1.0 mPa·s to 200 mPa·s.
7. The detergent for printing machine according to any one of claims 1 to 6 comprising a nonionic surfactant.
8. The detergent for printing machine according to claim 7, wherein the HLB of the nonionic surfactant is 10 or more and 20 or less.
9. The detergent for printing machine according to claim 7 or 8, wherein the nonionic surfactant has an ethylene oxide group.
10. The detergent for printing machine according to any one of claims 7 to 9, wherein the content of the nonionic surfactant is 5 mass% or more and 40 mass% or less.
11. The detergent for printing machine according to any one of claims 1 to 10, wherein the content of water is 40 mass%

or more and 99.99 mass% or less

12. The detergent for printing machine according to any one of claims 1 to 11 to be used for cleaning off an active energy ray-curable ink.

13. The detergent for printing machine according to claim 12, wherein the acid value of a resin contained in the active energy ray-curable ink is 30 mg KOH/g or more and 250 mg KOH/g or less.

14. The detergent for printing machine according to any one of claims 1 to 13, wherein the detergent for printing machine is a detergent for offset printing machine.

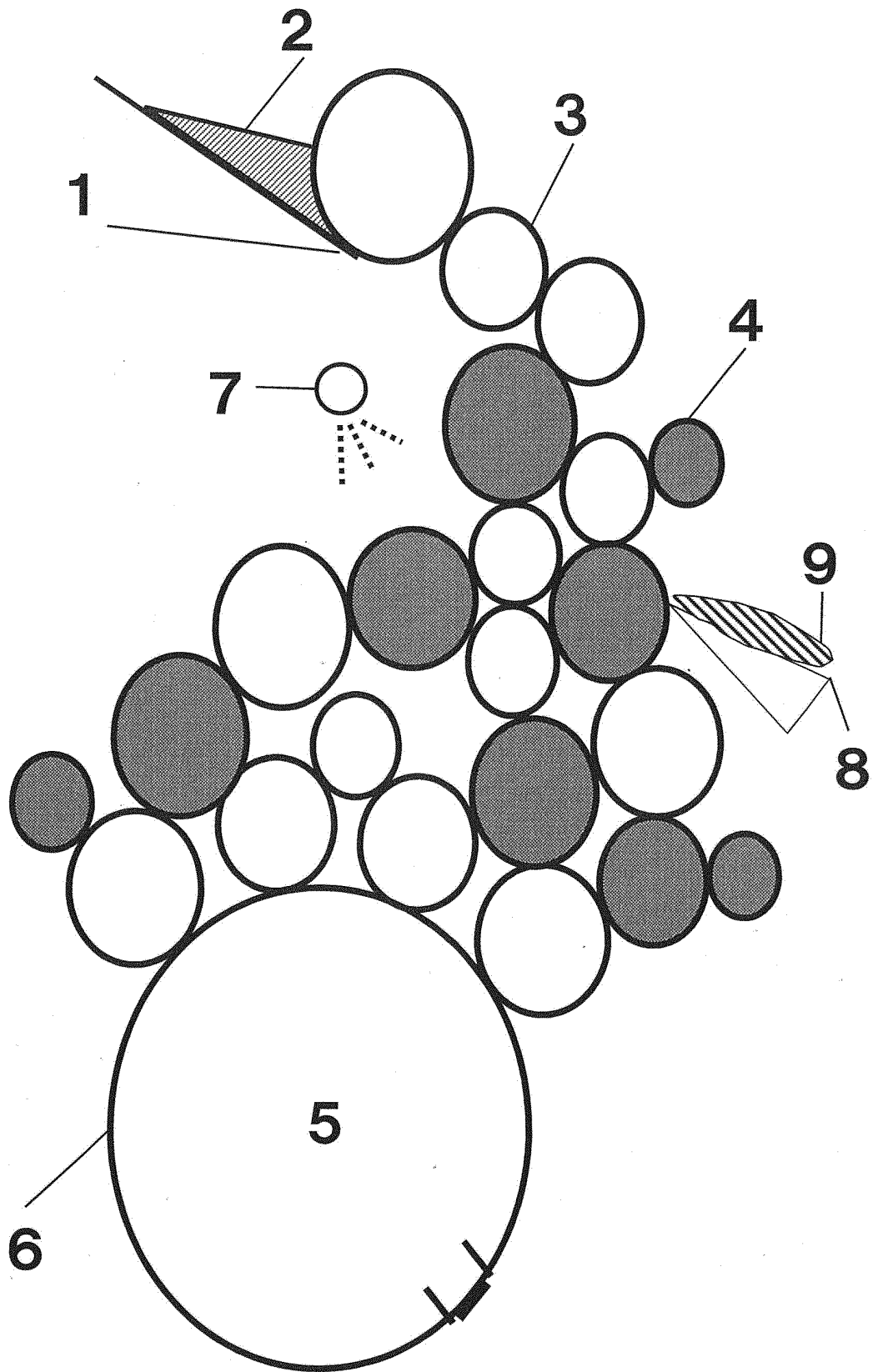
15. A method for cleaning off an active energy ray-curable ink using the detergent for printing machine according to any one of claims 1 to 14.

16. The method for cleaning off an active energy ray-curable ink using the detergent for printing machine according to claim 15, wherein the cleaning time is 10 min or less.

17. The method for cleaning off an active energy ray-curable ink according to claim 15 or 16, wherein the number of applications of the detergent in offset printing is 10 or less.

18. The method for cleaning off an active energy ray-curable ink according to claim 15 or 16, wherein the number of wipes required for washing off all ink in a washability evaluation in flexographic printing is two or less.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/002498

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B41F35/02 (2006.01) i, B41F35/06 (2006.01) i, C11D1/72 (2006.01) i,
C11D3/33 (2006.01) i

FI: C11D3/33, C11D1/72, B41F35/02, B41F35/06

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. B41F35/02, B41F35/06, C11D1/72, C11D3/33

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2020

Registered utility model specifications of Japan 1996-2020

Published registered utility model applications of Japan 1994-2020

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	[0034]-[0036], [0039], [0074], [0075], [0097]-[0100], [0123], examples E1, E3, E4	5, 8, 13, 16-18
X	JP 2016-056319 A (ISHIHARA CHEMICAL CO., LTD.) 21.04.2016 (2016-04-21), claims 1, 6, paragraph [0013],	1-3, 6
A	example no. 15, table 1	4-5, 7-18
X	JP 2016-060156 A (SAKATA INX CORPORATION) 25.04.2016 (2016-04-25), claim 1, example 8, table 1	1, 6, 11
A		2-5, 7-10, 12-18
Y	WO 2007/119392 A1 (ARAKAWA CHEM IND CO., LTD.) 25.10.2007 (2007-10-25), paragraph [0034]	5, 8, 13, 16-18
A		1-4, 6-7, 9-12, 14-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
20.02.2020

Date of mailing of the international search report
03.03.2020

Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/002498

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Form PCT/ISA/210 (second sheet) (January 2015)

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 [0038]-[0040], [0043],
 [0080], [0081], [0105]-[0108],
 [0135], examples E1, E3, E4
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