[Patent Document]

[0008]

[Patent Document 1] Japanese Patent Application Laid-Open No. 2008-143993 (Claims)

[Patent Document 2] Japanese Patent No. 4830224 (Claims)

[Summary of the Invention]

[Problems to Be Solved by the Invention]

[0009]

However, in the conventional active energy beam-curable offset printing inks disclosed in Patent Documents 1 and 2, sufficient curing was not accomplished at the printing speed actually used in the UV printer or by the amount of exposure in the case of power-saving UV, and the cured film suffered from insufficient water resistance. In addition, addition of a thixotropic agent was occasionally necessary to provide the ink with suitable printing adaptability (Patent Document 2). Furthermore, since the ink cures immediately after coating the ink on the substrate by an active energy beam, surface irregularities due to the insufficient ink levelling inviting decrease of the gloss value of the printed material compared to normal printed material occurred even if the curing was sufficient. In other words, ink viscosity had been increased by increasing the resin concentration in the lithographic ink to thereby improve the resistance to surface staining during the printing. However, increase of the viscosity of the lithographic ink results in the loss of the fluidity, and accordingly, the ink cures before the levelling of the ink in the active energy beam-curable printing wherein the ink instantaneously cures by the irradiation of an active energy beam. This resulted in the likeliness of surface irregularities on the film surface of the lithographic ink, and the printed material suffered from inferior gloss compared to the oil-based lithographic ink.

[0010]

In view of such situation, an object of the present invention is to obviate the problems of the prior art as described above and provide a lithographic ink which has a highly sensitive curability for active energy beam simultaneously with a high washability with water, and which also has excellent resistance to surface staining in the printing, high water resistance when cured into a cured film, and high gloss. Another object of the present invention is to provide a varnish constituting such lithographic ink and a method for producing printed materials by using such ink.

[Means for Solving the Problems]

[0011]

Accordingly, in an aspect, the present invention provides a lithographic ink of tip that comprises (a) a pigment and (b) a resin having an ethylenically unsaturated group and a hydrophilic group, and a surfactant as (g) a pigment dispersant wherein content of the pigment dispersant is 5 to 50 parts by mass in relation to 100 parts by mass of the pigment (a).

[0011a]

In another aspect, the present invention provides a varnish for a lithographic ink constituting the lithographic ink as described herein, wherein varnish comprises the polyfunctional (meth)acrylate having

hydroxyl group and a resin having a hydrophilic group.

[0011b] In another aspect, the present invention provides a method for producing a printed material using the lithographic ink as described herein.

[0011c]

In another aspect, the present invention provides a method for producing a printed material comprising the steps of coating the lithographic ink as described herein on a substrate and conducing irradiation with an active energy beam.

[0011d]

In another aspect, the present invention provides a method for producing a printed material comprising the step of printing the lithographic ink as described herein on a substrate by using a waterless lithography plate.

[0011e]

In yet another aspect, the present invention provides a method for producing a printed material comprising the step of printing the lithographic ink as described herein on a substrate by using a water lithography plate.

[Merits of the Invention]

[0012]

The present invention provides a lithographic ink which has a highly sensitive curability for active energy beam simultaneously with a high washability with water, and which also has excellent resistance to surface staining in the printing and high water resistance of the cured film. A printed material having excellent

resistance to surface staining of the lithographic ink, and preferably up to 10 mass %, more preferably up to 8 mass %, and still more preferably up to 5 mass % in view of the good storage stability of the lithographic ink.

[0101]

The lithographic ink of the present invention preferably contains a photopolymerization initiator (e) in order to improve curability of the ink, and also, a sensitizing agent to assist the effect of the photopolymerization initiator (e). Examples of such photopolymerization initiator (e) include the following types which are different in the mechanism, namely, single molecule direct cleavage type, intra-ion pair electron transfer type, hydrogen atom abstraction type, and two molecule complex type photopolymerization initiators, and the photopolymerization initiator used may be selected from these types.

[0102]

The photopolymerization initiator (e) used in the present invention is preferably those generating an reactive radical, and examples include benzophenone, o-benzoyl methyl benzoate, 4,4-bis(dimethylamine)benzophenone, 4,4-bis(diethylamino)benzophenone, 4,4-dichlorobenzophenone, 4-benzoyl-4-methyl diphenyl ketone, dibenzyl ketone, fluorenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenyl-2-phenylacetophenone, 2-hydroxy-2-methylpropiophenone, p-t-butyldichloroacetophenone, thioxanthone, 2-methylthioxanthone, 2-chlorothioxanthone, 2-isopropylthioxanthone, diethylthioxanthone, benzyl, benzyldimethylcetanol, benzyl methoxyethyl acetal, benzoin, benzoin methyl ether, benzoin butyl ether, anthraquinone, 2-t-butylanthraquinone, 2-amylanthraquinone, β-chloroanthraquinone, anthrone, benzanthrone, dibenzosuberone, methylene anthrone, 4-azidobenzalacetophenone, 2,6-bis(p-azidobenzylidene)cyclohexanone, 2,6-bis(p-azidobenzylidene)-4-methyl cyclohexanone, 2-phenyl-1,2-butadione-2-(o-methoxycarbonyl)oxime, 1-phenyl-propanedione-2-(o-ethoxycarbonyl)oxime, 1,3-diphenyl-propanetrione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-3-ethoxy-propanetrione-2-(o-benzoyl)oxime, Michler's ketone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propanone, naphthalene sulfonyl chloride, quinoline sulfonyl chloride, N-phenylthioacridone, 4,4-azobisisobutyronitrile, diphenyl disulfide, benzthiazole disulfide, triphenylphosphine, camphorquinone, carbon tetrabromide, tribromophenyl sulfone, benzoin peroxide, and a combination of photo-reductive die such as eosin or methylene blue and a reducing agent such as ascorbic acid or triethanolamine.

[0103]

Examples of the sensitizing agent include 2,4-diethylthioxanthone, isopropylthioxanthone, 2,3-bis(4-diethylaminobenzal)cyclopentanone, 2,6-bis(4-dimethylaminobenzal)cyclohexanone, 2,6-bis(4-dimethylaminobenzal)-4-methylcyclohexanone, Michler's ketone, 4,4-bis(diethylamino)-benzophenone, 4,4-bis(dimethylamino)chalcone, 4,4-bis(diethylamino)chalcone, p-dimethylaminocinnamylidene indanone, p-dimethylaminobenzylidene indanone, 2-(p-dimethylamino phenyl vinylene)-isonaphthothiazole, 1,3-bis(4-dimethylaminobenzal)acetone, 1,3-carbonyl-bis(4-diethylaminobenzal)acetone, 3,3-carbonyl-bis(7-diethylamino coumarin), N-phenyl-N-ethyl ethanolamine, N-phenylethanolamine, N-tolyldiethanolamine, isoamyl dimethylaminobenzoate, isoamyl diethylaminobenzoate, 3-phenyl-5-benzoylthiotetrazole, and

alkyl ether phosphate, polyoxyethylene tridecyl ether phosphate, and polyoxyethylene lauryl ether phosphate.

[0117]

The pigment dispersant (g) preferably has a basic group in addition to the acidic group. Inclusion of the basic group is preferable since the basic group in the pigment dispersant (g) contributes for improving the effect of suppressing the pigment agglutination. Examples of the basic group of the pigment dispersant (g) include functional groups containing nitrogen element such as amino group, amide group, azo group, and cyano group, and most preferred is the pigment dispersant containing amino group.

[0118]

The amine value of the pigment dispersant (g) is preferably 5 to 50 mgKOH/g. When the amine value of the pigment dispersant (g) is at least 5 mgKOH/g, the pigment dispersant (g) becomes more likely to be adsorbed by the pigment having an acidic group, and the effect of preventing the pigment agglutination will be improved. In the meanwhile, use of the pigment dispersant (g) having an amine value of up to 50 mgKOH/g enables prevention of viscosity increase by the interaction with the ethylenically unsaturated group-containing resin having an acidic group. When the amine value of the pigment dispersant (g) is in such range, agglutination of the pigment can be suppressed to improve the ink fluidity. As a consequence, the ink will have an improved levelling property, and the printed material prepared by using such ink will enjoy an improved gloss.

[0119]

The amine value of the pigment dispersant (g) may be determined according to the method described in “4.1 electrical potentiometric titration” in JIS K 7237: 1995 “Testing method for total amine values of amine-based hardeners of epoxide resins”.

[0120]

Content of the pigment dispersant (g) of the present invention is preferably 5 to 50 parts by mass in relation to 100 parts by mass of the pigment (a). Content of the pigment dispersant (g) of at least 5 parts by mass is preferable in view of improving the effect for suppressing the pigment agglutination. In the meanwhile, content of the pigment dispersant (g) of up to 50 parts by mass is preferable in view of preventing loss of the effect for preventing the pigment agglutination. The effect of suppressing the pigment agglutination is improved by the content of the pigment dispersant (g) within such range.

[0121]

The lithographic ink of the present invention preferably contains water. When water is included in the ink, adjustment of the ink viscosity is facilitated, and volume of the VOC discharged in the printing will be reduced, and consequently, production of a printed material without causing serious burden on the environment will be enabled. In addition, production of the lithographic ink of the present invention will be enabled at a reduced cost.

[0122]

Content of water in the lithographic ink of the present invention is preferably at least 5 mass %. When the water content is in such range, the ink will exhibit good washability with water, and simultaneously,

Pigment 1: Seika cyanine blue 4920 (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

Photopolymerization initiator 1: “IRGACURE” (Registered Trademark) 907 (manufactured by BASF)

Photopolymerization initiator 2: “IRGACURE” (Registered Trademark) TPO-L (manufactured by BASF)

Sensitizing agent 1: diethylaminobenzophenone (manufactured by Tokyo Chemical Industry Co., Ltd.)

Additive 1: lauryl acrylate (manufactured by Wako Pure Chemical Industries, Ltd.)

Wax 1: PTFE wax, KTL-4N (manufactured by KITAMURA LIMITED)

[0208]

<Waterless lithography test>

A waterless lithography plate (TAN-E manufactured by Toray Industries, Inc.) was mounted on an offset press (Oliver 266EPZ manufactured by SAKURAI GRAPHIC SYSTEMS CORPORATION), and 5000 coated papers were printed by using inks respectively having the composition of Examples 18 to 26, Reference Examples 1 to 3, and Comparative Examples 9 to 11. The ink was cured by UV irradiation using a UV irradiation apparatus manufactured by Ushio (120 W/cm, 1 ultra-high pressure metal halide lamp) at a belt conveyer speed of 80 m/min to obtain the printed material. The evaluation method was as described below.

[0209]

<Water lithography test>

A water lithography plate (XP-F manufactured by FUJIFILM Corporation) was mounted on an offset press (Oliver 266EPZ, manufactured by SAKURAI GRAPHIC SYSTEMS CORPORATION), and 5000 coated papers were printed with inks respectively having the composition of Examples 27 to 29, Reference Examples 4, and Comparative Examples 12 and 13 by using tap water admixed with 3 weight% of an etching solution (SOLAIA-505, manufactured by T&K TOKA) for the wetting water. The ink was cured by UV irradiation using a UV irradiation apparatus manufactured by Ushio (120 W/cm, 1 ultra-high pressure metal halide lamp) at a belt conveyer speed of 80 m/min to obtain the printed material.

[0210]

<Ink evaluation>

(1) Viscosity

A cone plate (cone angle, 1°; diameter, 40 mm) was mounted on Rheometer-MCR301 manufactured by Anton Paar, and the viscosity at 25°C and 0.5 rpm was measured for 0.15 ml of the ink measured by an ink pipette.

[0211]

[0225]

[Example 27] <Preparation of the water lithographic ink>

The procedure of Example 18 was repeated except that the composition was as shown in Table 5 and the emulsifier 1 was added to prepare the lithographic ink of Example 27. The resulting lithographic ink had a viscosity at 0.5 rpm of 66 Pa.s. The resistance to surface staining was excellent with the reflection density in the non-printing area of 0.02. The resulting printed material had an excellent gloss in the solid part of 36.

[0228]

<Starting materials for the ink>

[Type of the Document] Claims

[Claim 1]

A lithographic ink comprising (a) a pigment and (b) a resin having an ethylenically unsaturated group and a hydrophilic group, and a surfactant as (g) a pigment dispersant wherein content of the pigment dispersant is 5 to 50 parts by mass in relation to 100 parts by mass of the pigment (a).

[Claim 2]

A lithographic ink according to claim 1 wherein the ink is curable by an active energy beam.

[Claim 3]

A lithographic ink according to claim 1 or 2 wherein the hydrophilic group of the resin (b) having an ethylenically unsaturated group and a hydrophilic group includes at least one functional group selected from carboxyl group, sulfo group, phosphate group, hydroxy group, and amino group.

[Claim 4]

A lithographic ink according to claim 1 or 2 wherein the hydrophilic group of the resin (b) having an ethylenically unsaturated group and a hydrophilic group includes carboxyl group.

[Claim 5]

A lithographic ink according to claim 1 or 2 wherein the hydrophilic group of the resin (b) having an ethylenically unsaturated group and a hydrophilic group includes carboxyl group and hydroxy group.

[Claim 6]

A lithographic ink according to any one of claims 1 to 5 wherein the hydrophilic group of the resin (b) having an ethylenically unsaturated group and a hydrophilic group has an acid value of at least 30 mgKOH/g and up to 250 mgKOH/g.

[Claim 7]

A lithographic ink according to any one of claims 1 to 6 wherein the hydrophilic group of the resin (b) having an ethylenically unsaturated group and a hydrophilic group has an iodine number of at least 0.5 mol/kg and up to 3.0 mol/kg.

[Claim 8]

A lithographic ink according to any one of claims 1 to 7 wherein the resin (b) having an ethylenically unsaturated group and a hydrophilic group contains at least one resin selected from acrylic resin, styrene acrylic resin, and styrene maleic acid resin.

[Claim 9]

A lithographic ink according to any one of claims 1 to 8 wherein the resin (b) having an ethylenically unsaturated group and a hydrophilic group has a weight average molecular weight of at least 20,000 and up to 100,000.

[Claim 10]

A lithographic ink according to any one of claims 1 to 9 further comprising (c) a reactive diluent.

[Claim 11]

A lithographic ink according to claim 10 wherein the reactive diluent (c) is a hydrophilic

polyfunctional (meth)acrylate.

[Claim 12]

A lithographic ink according to claim 10 or 11 wherein the reactive diluent (c) is a polyfunctional (meth)acrylate having hydroxyl group.

[Claim 13]

A lithographic ink according to claim 12 wherein the polyfunctional (meth)acrylate having hydroxyl group has a hydroxy group value of at least 50 mgKOH/g and up to 200 mgKOH/g.

[Claim 14]

A lithographic ink according to claim 12 or 13 wherein the polyfunctional (meth)acrylate having hydroxyl group has a molecular weight of at least 100 and up to 1000.

[Claim 15]

A lithographic ink according to any one of claims 12 to 14 wherein the polyfunctional (meth)acrylate having hydroxyl group includes at least one member selected from pentaerythritol tri(meth)acrylate, diglycerin tri(meth)acrylate, and ditrimethylolpropane tri(meth)acrylate.

[Claim 16]

A lithographic ink according to any one of claims 1 to 15 further comprising (e) a photopolymerization initiator.

[Claim 17]

A lithographic ink according to any one of claims 1 to 16 wherein the pigment dispersant (g) has an acidic group.

[Claim 18]

A lithographic ink according to any one of claims 1 to 17 wherein the pigment dispersant (g) has at least one functional group selected from carboxyl group, sulfo group, and phosphate group.

[Claim 19]

A lithographic ink according to claim 17 or 18 wherein the pigment dispersant (g) has an acid value of 5 to 200 mgKOH/g.

[Claim 20]

A lithographic ink according to any one of claims 17 to 19 wherein the pigment dispersant (g) also has a basic group.

[Claim 21]

A lithographic ink according to any one of claims 17 to 20 wherein the pigment dispersant (g) has amino group.

[Claim 22]

A lithographic ink according to claim 21 or 22 wherein the pigment dispersant (g) has an amine value of 5 to 50 mgKOH/g.

[Claim 23]

A lithographic ink according to any one of claims 1 to 22 wherein the pigment (a) is a water-insoluble salt.

[Claim 24]

A lithographic ink according to any one of claims 1 to 23 wherein the pigment (a) is an azo lake pigment.

[Claim 25]

A lithographic ink according to any one of claims 1 to 23 wherein the pigment (a) is a metal complex.

[Claim 26]

A lithographic ink according to any one of claims 1 to 22 wherein the pigment (a) is carbon black.

[Claim 27]

A lithographic ink according to claim 26 wherein the carbon black has an acidic group.

[Claim 28]

A lithographic ink according to claim 26 or 27 wherein the carbon black has an average particle diameter of 10 to 50 nm.

[Claim 29]

A lithographic ink according to any one of claims 26 to 28 wherein dibutyl phthalate absorption per 100 g of the carbon black is 40 to 80 cm^3/100 g.

[Claim 30]

A lithographic ink according to any one of claims 1 to 29 wherein the ink comprises (d) at least one compound selected from silicone liquid, alkyl acrylate, hydrocarbon solvent, and fluorocarbon.

[Claim 31]

A varnish for a lithographic ink constituting the lithographic ink according to any one of claims 1 to 30 wherein varnish comprises the polyfunctional (meth)acrylate having hydroxyl group and a resin having a hydrophilic group.

[Claim 32]

A varnish for a lithographic ink according to claim 31 wherein content of the polyfunctional (meth)acrylate having hydroxyl group in the varnish for lithographic ink is at least 40 mass % and up to 90 mass %.

[Claim 33]

A method for producing a printed material using the lithographic ink according to any one of claims 1 to 30.

[Claim 34]

A method for producing a printed material comprising the steps of coating the lithographic ink according to any one of claims 1 to 30 on a substrate and conducing irradiation with an active energy beam.

[Claim 35]

A method for producing a printed material comprising the step of printing the lithographic ink

according to any one of claims 1 to 30 on a substrate by using a waterless lithography plate.

[Claim 36]

A method for producing a printed material comprising the step of printing the lithographic ink according to any one of claims 1 to 30 on a substrate by using a water lithography plate.

[Claim 37]

A method for producing a printed material according to claim 35 or 36 further comprising the step of conducing irradiation with an active energy beam.

[Claim 38]

A method for producing a printed material according to any one of claims 34 to 37 wherein the substrate comprises at least one member selected from plastic film, plastic film laminate paper, metal, metal-vapor-deposited paper, and metal-vapor-deposited plastic film.

[Claim 39]

A method for producing a printed material according to claim 34, 37, or 38 wherein the active energy beam is an electron beam or LED-UV.