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(11)

EP 3 950 368 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

09.02.2022 Bulletin 2022/06

(51) International Patent Classification (IPC):

B41M 1/06 ^(2006.01) **B41M 1/30** ^(2006.01)
B41N 3/08 ^(2006.01)

(21) Application number: **20783488.8**

(52) Cooperative Patent Classification (CPC):

B41M 1/06; B41M 1/30; B41N 3/08

(22) Date of filing: **05.03.2020**

(86) International application number:

PCT/JP2020/009369

(87) International publication number:

WO 2020/203013 (08.10.2020 Gazette 2020/41)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

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(54) **METHOD FOR MANUFACTURING PRINTED MATTER**

(57) The present invention provides a method for producing printed matter that serves to achieve improved adhesion of an ink to a base material.

The method for producing printed matter according to the present invention is a method for producing printed

matter using a lithographic printing plate characterized in that an active energy ray curable lithographic ink is applied to a base material and exposed to radiation and that a dampening solution having a dissolved oxygen concentration of 5 ppm or less is used.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a process for producing printed matter.

BACKGROUND ART

10 **[0002]** With the increase in the global population, demand for flexible packaging materials intended mainly for packaging of food products and daily necessities is expected to continue to grow. Gravure printing, which is currently the mainstream in the printing of flexible packaging materials, can produce printed matter with a vivid appearance. However, since gravure printing uses ink having a large solvent content, a large amount of energy is required for drying the ink solvent and treating the discharged air, which causes a heavy environmental load. Furthermore, as market needs are changing from conventional mass production and mass consumption to high-mix low-volume manufacturing and short delivery times, gravure printing, which is excel in large lot production, is now an expensive process requiring increased production costs due to costly plates and plate making. Therefore, attempts have begun in recent years to enable the printing of flexible wrapping materials by the lithographic printing technique, which is less expensive in terms of costs for plates and plate making and is superior in terms of low-volume manufacturing and short delivery time (Patent document 1).

15 **[0003]** Lithographic printing is a printing method that is widely used for supplying printed matter at high speed, in large quantities, and at low cost. In addition, in recent years, there has been an increasing demand for reduction in volatile components contained in lithographic inks in order to deal with environmental problems. For this reason, the use of lithographic inks that are free of volatile components and able to be cured instantly by irradiation with active energy rays (hereinafter referred to as active energy ray curable lithographic inks) is now being promoted. For the printing of flexible packaging materials, a roll-to-roll printing machine is generally adopted and accordingly, quick-drying property of the ink is important. In addition to environmental advantages, active energy ray curing type lithographic printing, which uses an active energy ray curable lithographic ink, has energy saving and high productivity features because it does not require thermal energy and serves to shorten the drying step.

20 **[0004]** Furthermore, since such flexible printed packaging materials are mainly intended for the packaging of food products, it is desirable for the radiation curable lithographic ink to be free of polymerization initiators from the viewpoint of preventing the contamination of the contents.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

25 **[0005]** [Patent document 1] Japanese Unexamined Patent Publication (Kokai) No. 2004-358788

SUMMARY OF THE INVENTION

40 PROBLEM TO BE SOLVED BY THE INVENTION

[0006] However, in general, radiation curable lithographic inks are low in adhesiveness to base materials and cannot develop sufficiently strong adhesion to base materials as compared with gravure printing.

45 **[0007]** To solve this problem, the present invention provides a method for producing printed matter that can ensure improved adhesion between the ink and the base material even when the ink used is an active energy ray curable lithographic ink.

MEANS FOR SOLVING THE PROBLEM

50 **[0008]** As a result of intensive studies aiming to solve the above problem, the present inventors found that the problem can be solved by using a dampening solution having a decreased dissolved oxygen concentration. Specifically, the present invention has a constitution as described below.

[0009] A method for producing printed matter using a lithographic printing plate characterized in that an active energy ray curable lithographic ink is transferred onto a base material and exposed to radiation and that a dampening solution having a dissolved oxygen concentration of 5 ppm or less is used.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0010] The method for producing printed matter according to the present invention serves to achieve improved adhesion of an ink to a base material.

DESCRIPTION OF EMBODIMENTS

[0011] The invention is described specifically below.

[0012] For the present invention, the term "active energy ray curable lithographic ink" refers to an ink before being cured and the term "ink" refers to an ink after being cured.

[0013] A method for producing printed matter according to the present invention relates to a method for producing printed matter using a lithographic printing plate characterized by comprising a step for transferring an active energy ray curable lithographic ink onto a base material and exposing it to radiation. More specifically, it relates to a method for producing printed matter using a lithographic printing plate characterized by attaching a dampening solution to the non-image area of a lithographic printing plate while attaching an active energy ray curable lithographic ink to the image area of the lithographic printing plate and transferring it to a base material, followed by exposure to radiation.

[0014] The method for producing printed matter according to the present invention is characterized by using a dampening solution having a dissolved oxygen concentration of 5 ppm or less. In the printing process, as the active energy curable lithographic ink and the dampening solution, which are located adjacent to each other on a lithographic printing plate, come into contact with each other, the dampening solution is emulsified with the active energy curable lithographic ink and dispersed in the active energy curable lithographic ink. Accordingly, with an increasing concentration of dissolved oxygen in the dampening solution, radicals generated on the surface of the base material by exposure to radiation are more easily captured by the dissolved oxygen and deactivated thereby. In a normal dampening solution, the dissolved oxygen concentration is around 10 ppm in order to allow the solution temperature to be maintained at a low temperature of around 15°C. For the method for producing printed matter according to the present invention, on the other hand, radical deactivation can be depressed by reducing the dissolved oxygen concentration in the dampening solution at 1 atm and 15°C to 5 ppm or less, and as a result, radical crosslinking between the active energy ray curable lithographic ink and the base material is accelerated to ensure increased adhesion of the ink to the base material. The dissolved oxygen concentration is more preferably 1 ppm or less. Good methods for reducing the dissolved oxygen concentration in a dampening solution include a bubbling based method that uses an inert gas such as nitrogen and argon, a degassing based method that performs separation using a hollow fiber membrane, and a method that uses a deoxidation apparatus. Furthermore, these methods may be combined to reduce the dissolved oxygen concentration in a dampening solution. The use of a bubbling based method is preferable because such a method requires only a simple procedure to realize a reduction in the dissolved oxygen concentration in the dampening solution to 5 ppm or less. The use of a degassing based method is more preferable because the dissolved oxygen concentration in the dampening solution can be reduced to 1 ppm or less. The dissolved oxygen concentration in the dampening solution should preferably as low as possible for the above reasons, but from the viewpoint of the detection sensitivity of available measuring instruments, it is preferably 0.01 ppm or more.

[0015] In addition, it is also preferable for the dampening solution to be substantially free of antioxidants. Being substantially free of antioxidants means that antioxidants preferably account for 0.05 mass% or less, and more preferably 0.01 mass% or less. Normally, a dampening solution contains an antioxidant in order to suppress the sensitization of the printing plate. The term "sensitization" used here means oxidation of aluminum in the non-image area of a printing plate, which leads to a decrease in hydrophilicity. Such oxidation occurs due to the addition of oxygen atoms to radicals generated in chemical compounds. Since an antioxidant has a stronger radical scavenging ability than oxygen, it is preferable for the dampening solution to be substantially free of antioxidants. When the dampening solution in use is substantially free of antioxidants, radical crosslinking between the active energy ray curable lithographic ink and the base material proceeds, which serves to increase the adhesion of the ink to the base material.

[0016] For the present invention, examples of good antioxidants include phenol based, amine based, and phosphorus based organic antioxidants, metal based antioxidants, and natural product derived antioxidants. Examples of the phenol based antioxidants include 2,6-di-*t*-butyl-*p*-cresol, 2,6-diphenyl-4-octaocadesiloxyphe-*nol*, stearyl-(2,5-dimethyl-4-hydroxybenzyl) thioglycolate, stearyl- β -(4-hydroxy-3,5-di-*t*-butylphenyl) propionate, distearyl-3,5-di-*t*-butyl-4-hydroxybenzyl phosphonate, triethylene glycol bis[β -(3-*t*-butyl-4-hydroxy-5-methylphenyl) propionate], 3,9-bis[1,1-dimethyl-2-(β -3-*t*-butyl-4-hydroxy-5-methylphenyl) propionyloxy ethyl]-2,4,8,10-tetraoxaspiro[5.5] undecane, 2,2'-methylene bis(4-methyl-6-*t*-butylphenol), bis[3,5-bis(4-hydroxy-3-*t*-butylphenyl) butyric acid] glycol ester, bis[2-*t*-butyl 4-methyl-6-(2-hydroxy-3-*t*-butyl-5-methylbenzyl)phenyl] terephthalate, 2-*t*-butyl 4-methyl-6-(2-hydroxy-3-*t*-butyl-5-methylbenzyl) phenyl acrylate, and 1,3,5-tris- β -(3,5-di-*t*-butyl 4-hydroxyphenyl) propionyloxy ethyl isocyanurate.

[0017] Examples of the amine based antioxidants include monoalkyl diphenylamines, dialkyl diphenylamines, polyalkyl diphenylamines, and alkyl substituted phenyl- α -naphthylamines, whose alkyl groups contain 1 to 10 carbon atoms. More

specifically, they include monobutyl diphenylamine, monooctyl diphenylamine, monononyl diphenylamine, 4,4'-dibutyl diphenylamine, 4,4'-dipentyl diphenylamine, 4,4'-dihexyl diphenylamine, 4,4'-diheptyl diphenylamine, 4,4'-dioctyl diphenylamine, 4,4'-dinonyl diphenylamine, 4-butyl-4'-octyl diphenylamine, tetrabutyl diphenylamine, tetrahexyl diphenylamine, tetraoctyl diphenylamine, tetranonyl diphenylamine, di(2,4-diethylphenyl)amine, di(2-ethyl-4-nonylphenyl)amine, methylphenyl- α -naphthylamine, ethylphenyl- α -naphthylamine, butylphenyl- α -naphthylamine, hexylphenyl- α -naphthylamine, heptylphenyl- α -naphthylamine, octylphenyl- α -naphthylamine, nonylphenyl- α -naphthylamine, dodecylphenyl- α -naphthylamine, and phenyl- α -naphthylamine.

[0018] Examples of the phosphorus based antioxidants include triphenyl phosphite, tris-(nonylphenyl) phosphite, tris-(monononylphenyl) phosphite, tris-(dinonylphenyl) phosphite, tris-(2,4-dibutylphenyl) phosphite, octyldiphenyl phosphite, tetraalkyl bisphenol Adiphosphite, tetra(tridecyl)-4,4'-butylidene bis(3-methyl-6-*t*-butylphenol) diphosphite, hexa(tridecyl)-1,1,3-tris-(2-methyl-5-*t*-butyl-4-hydroxyphenyl) butane triphosphite, bis(nonylphenyl) pentaerythritol diphosphite, phenyl-bisphenol A pentaerythritol diphosphite, bis(2,4-di-*t*-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-*t*-butyl-4-methylphenyl) pentaerythritol diphosphite.

[0019] Examples of the metal based antioxidants include zinc based or molybdenum based antioxidants. More specifically, they include zinc dithiophosphate, molybdenum dialkyldithiophosphate, and molybdenum dithiocarbamate.

[0020] Examples of the natural product derived antioxidants include tocopherol, L-ascorbyl stearate, and L-ascorbyl palmitate.

[0021] For the method for producing printed matter according to the present invention, examples of good radiation sources include electron beam and gamma ray. Radiation generates high energy secondary electrons in the irradiated substance, excites surrounding molecules, and produces reaction-active species such as radicals. Depending on the chemical structure of the irradiated substance, the resulting reaction active species can cause various reactions such as crosslinking and decomposition. If the material being irradiated is assumed to be an active energy ray curable lithographic ink, radicals are generated in the active energy ray curable lithographic ink to accelerate radical polymerization, resulting in the formation of a cured ink film. Radiation also acts on the base material after passing through the transferred active energy ray curable lithographic ink. In the polymer present in the base material as well, radicals are generated to cause reactions such as molecular crosslinking and decomposition. In particular, as radical polymerization proceeds between the active energy ray curable lithographic ink and the base material, covalent bonds are formed between the ink and the base material to develop strong adhesion.

[0022] In a dampening solution, it is preferable for water to account for 90 mass% to 99 mass%.

[0023] A dampening solution preferably contains an acid to have a pH value in the acid range. Specific examples of the acid include acetic acid, citric acid, oxalic acid, malic acid, tartaric acid, lactic acid, ascorbic acid, gluconic acid, hydroxyacetic acid, malonic acid, sulfanilic acid, *p*-toluenesulfonic acid, organic phosphonic acid, phosphoric acid, nitric acid, sulfuric acid, polyphosphoric acid. Furthermore, the dampening solution can develop a buffering ability if it additionally contains an alkali metal salt, alkaline earth metal salt, ammonium salt, organic amine salt, etc., of these acids.

[0024] The dampening solution can also contain alcohols and glycols in order to decline in dynamic surface tension and improve in wettability on the printing plate surface. Specific examples include 3-methyl-1-butyn-3-ol, 2-butyne-1,4-diols, 3-methyl-1-pentyn-3-ol, 2,5-dimethyl-3-hexyne-2,5-diol, 3,5-dimethyl-1-hexyn-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and 2,5,8,11-tetramethyl-6-dodecyne-5,8-diol, as well as ethylene oxide adducts and propylene oxide adducts thereof.

[0025] The radiation used for the present invention is preferably an electron beam. In particular, it is preferable to use an electron beam with a low acceleration voltage because it normally is so low in penetrating power that it serves to apply energy intensively to the surface layer of an object, requires no special qualifications for its use, and can be handled easily. The penetration depth of an electron beam depends on the acceleration voltage, and it is preferably 50 kV or more, more preferably 90 kV or more, and still more preferably 110 kV or more, to allow a sufficient dose to be transmitted through the ink film. In addition, it is preferably 300 kV or less, more preferably 200 kV or less, and still more preferably 150 kV or less, because the dose given to the interior of the base material increases with an increasing penetrating depth. Furthermore, an electron beam with a higher irradiation intensity acts to generate a larger amount of radical species in the target material to cause a greater damage to the base material and accordingly, the irradiation intensity is preferably 10 kGy or more and 100 kGy or less, and more preferably 20 kGy or more and 50 kGy or less.

[0026] It is preferable for the base material used for the present invention to be a plastic film. Examples of the plastic film include films of plastics such as polyethylene, polyester, polyamide, polyimide, polyalkyl (meth)acrylate, polystyrene, poly- α -methylstyrene, polypropylene, polycarbonate, polyvinyl alcohol, polyvinyl acetal, polyvinyl chloride, and polyvinylidene fluoride, plastic film laminated papers composed of paper sheets laminated with plastic films such as listed above, and metal deposited plastic films composed of plastic films having deposited metals such as aluminum, zinc, and copper. It is preferable to adopt a plastic film containing a radiation crosslinkable polymer, more preferably a plastic film in which a radiation crosslinkable polymer is localized near the outermost surface. Here, a radiation crosslinkable polymer is a polymer that undergoes a crosslinking reaction, instead of being decomposed, when exposed to radiation. Specifically, its examples include polyethylene, polyester, polyamide, polyalkyl acrylate, polystyrene, polypropylene,

polyvinyl alcohol, polyvinyl chloride, and polyvinylidene fluoride, of which particularly preferred are polyethylene, polyester, and polyamide, which have been generally used as base materials for printed flexible packages.

[0027] Furthermore, it is preferable for these plastic films to have an adhesive coated or a corona treated surface. As the plastic film used has an outermost surface that generates more radicals when exposed to radiation, more covalent bonds are formed by radical polymerization between the ink and the base material, serving to realize stronger adhesion. Preferred examples of adhesive coats include acrylic coats and urethane coats. In particular, it is more preferable to adopt an acrylic coat, which contains an acrylic group, that is, a functional group that easily generates radicals when irradiated with an electron beam.

[0028] The thickness of the base material is preferably 5 μm or more, and more preferably 10 μm or more, from the viewpoint of the mechanical strength of the base material required for printing. It is preferably 50 μm or less, and more preferably 30 μm or less, to ensure low base material cost.

[0029] It is preferable that the active energy ray curable lithographic ink used for the present invention contain a resin that has an ethylenically unsaturated group because it will work to increase the reactivity with radicals existing on the film surface, which serves to further improve the adhesion.

[0030] Examples of the resin having an ethylenically unsaturated group include acrylic resin, styrene-acrylic resin, styrene-maleic acid resin, rosin modified maleic acid resin, rosin modified acrylic resin, epoxy resin, polyester resin, polyurethane resin, and phenol resin, whose ethylenically unsaturated groups are introduced in their side chains, as well as phthalate resins. For example, an acrylic resin, styrene-acrylic resin, or styrene-maleic acid resin having an ethylenically unsaturated group can be produced by the procedure described below. Specifically, appropriate compounds selected from the group consisting of carboxyl group-containing monomers such as (meth)acrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, and anhydrides thereof, hydroxyl group-containing monomers such as 2-hydroxyethyl (meth)acrylate, amino group-containing monomers such as dimethylaminoethyl (meth)acrylate, mercapto group-containing monomers such as (meth)acrylic acid-2-(mercaptoacetoxyl) ethyl, sulfo group-containing monomers such as (meth)acrylamide-t-butylsulfonic acid, phosphoric acid group-containing monomers such as 2-(meth)acryloyloxy ethyl acid phosphate, and others such as (meth)acrylic esters, styrene, (meth)acrylonitrile, and vinyl acetate are polymerized or copolymerized using a radical polymerization initiator to produce a resin having a hydrophilic group. Then, a glycidyl group- or isocyanate group-containing ethylenically unsaturated compound, acrylic acid chloride, methacrylic acid chloride, or allyl chloride is added, through an addition reaction, to the active hydrogen-containing group, such as mercapto group, amino group, hydroxy group, and carboxy group, in the aforementioned hydrophilic group-containing resin to produce a resin having an ethylenically unsaturated group. It is noted, however, that the present invention is not limited to these methods.

[0031] Specific examples of the ethylenically unsaturated compound having a glycidyl group include glycidyl (meth)acrylate, allyl glycidyl ether, glycidyl crotonate, and glycidyl isocrotonate.

[0032] Specific examples of the ethylenically unsaturated compound having an isocyanate group include (meth)acryloyl isocyanate and (meth)acryloylethyl isocyanate.

[0033] A phthalate resin can be produced by either diallyl orthophthalate or diallyl isophthalate, or a mixture of both is subjected to a polymerization reaction in the presence of a polymerization initiator in an organic solvent. In this reaction, an unreacted portion containing ethylenically unsaturated groups will remain in the resin. As the phthalate resin, a commercially available product may be used instead of such a synthesized compound, and specific examples thereof include the Daiso DAP (registered trademark) series and Daiso ISODAP (registered trademark) manufactured by Osaka Soda Co., Ltd.

[0034] It is preferable for the resin having an ethylenically unsaturated group to have an acrylic equivalent of 300 g/eq or more and 2,000 g/eq or less because this ensures improved sensitivity and high storage stability. For the present Description, the acrylic equivalent (g/eq) of a resin is represented by the bromine number of the ink (the weight in grams of bromine that can be added to the unsaturated components in 100 g of a specimen) converted in terms of the weight in grams of the ink per mole of the acryloyl group, which is determined according to JIS K 2605.

[0035] It is preferable for the resin having an ethylenically unsaturated group to have a weight average molecular weight of 5,000 or more and 100,000 or less, which serves to allow the active energy ray curable lithographic ink to maintain a desirable printability. Here, the weight average molecular weight of a resin can be determined by gel permeation chromatography (GPC) and represented in terms of polystyrene.

[0036] For the method for producing printed matter according to the present invention, it is preferable for the resin having an ethylenically unsaturated group to account for 5 mass% or more and 40 mass% or less in the active energy ray curable lithographic ink because it serves to maintain a desirable printability.

[0037] Specific examples of commercially available products of active energy ray curable lithographic inks include EC DEVELOPMENT manufactured by Sun Chemical and XCURA EVO manufactured by Flint.

[0038] An active energy ray curable lithographic ink can be produced by dissolving a resin in a polyfunctional (meth)acrylate to prepare a resin varnish, adding a pigment and auxiliary agents, and kneading them in a three-roll mill.

[0039] Bifunctional examples of the polyfunctional (meth)acrylate include ethylene glycol di(meth)acrylate, diethylene

glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, and neopentyl glycol di(meth)acrylate. Trifunctional ones include trimethylolpropane tri(meth)acrylate, glycerin tri(meth)acrylate, and isocyanuric acid tri(meth)acrylate, as well as ethylene oxide addition products thereof and propylene oxide addition products thereof. Tetrafunctional ones include pentaerythritol tetra(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, and diglycerin tetra(meth)acrylate, as well as ethylene oxide addition products thereof and propylene oxide addition products thereof. Penta- or higher-functional ones include dipentaerythritol hexa(meth)acrylate, ethylene oxide addition products thereof, and propylene oxide addition products thereof. In addition, preferred examples of polyfunctional (meth)acrylates having hydroxy groups include poly(meth)acrylates of polyhydric alcohols such as trimethylolpropane, glycerin, pentaerythritol, diglycerin, ditrimethylolpropane, isocyanuric acid, and dipentaerythritol, as well as alkylene oxide addition products thereof. More specifically, they include trimethylolpropane di(meth)acrylate, glycerin di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, diglycerin di(meth)acrylate, diglycerin tri(meth)acrylate, ditrimethylolpropane di(meth)acrylate, ditrimethylolpropane tri(meth)acrylate, dipentaerythritol di(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, and dipentaerythritol penta(meth)acrylate, as well as ethylene oxide addition products thereof, propylene oxide addition products thereof, and tetraethylene oxide addition products thereof. Two or more of these may be contained in combination.

[0040] It is preferable for the active energy ray curable lithographic ink used for the present invention to contain a urethane compound because it can work to increase the contact with the base material. The aforementioned urethane compound means a compound that can be synthesized through a reaction between a polyisocyanate compound and a polyol compound, and from the viewpoint of curability in particular, it is preferable to use a urethane (meth)acrylate containing a (meth)acrylic group.

[0041] A urethane (meth)acrylate can be synthesized by reacting a hydroxyl group-containing (meth)acrylic ester, a polyisocyanate compound, and a polyol compound. There are no specific limitations on the hydroxyl group-containing (meth)acrylic ester, but good examples include poly(meth)acrylates of polyhydric alcohols such as trimethylolpropane, glycerin, pentaerythritol, diglycerin, ditrimethylolpropane, isocyanuric acid, and dipentaerythritol, as well as alkylene oxide addition products thereof. More specifically, they include trimethylolpropane di(meth)acrylate, glycerin di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, diglycerin di(meth)acrylate, diglycerin tri(meth)acrylate, ditrimethylolpropane di(meth)acrylate, ditrimethylolpropane tri(meth)acrylate, dipentaerythritol di(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, and dipentaerythritol penta(meth)acrylate, as well as ethylene oxide addition products thereof, propylene oxide addition products thereof, and tetraethylene oxide addition products thereof. Of these, pentaerythritol triacrylate is particularly preferred. These hydroxyl group-containing acrylic esters having two or more acrylic groups may be used singly or as a combination of two or more thereof.

[0042] It is preferable to use a diisocyanate as the polyisocyanate compound in order to control the viscosity of the urethane compound formed through a reaction between the hydroxyl group of a polyol compound and the isocyanate group of the polyisocyanate compound and to maintain a desirable compatibility with the resin or the monomer in the ink. There are no particular limitations on the diisocyanate, and good compounds having aromatic ring structures include toluene diisocyanate, diphenylmethane diisocyanate, and xylylene diisocyanate. Good compounds having alicyclic structures include isophorone diisocyanate, 4,4-methylenebiscyclohexyl diisocyanate, and hydrogenated xylylene diisocyanate. In addition, good compounds having aliphatic structures include hexamethylene diisocyanate. These diisocyanates may be used singly or as a mixture of two or more thereof.

[0043] Examples of the polyol compound include those having an ester structure, carbonate structure, or polyalkylene oxide structure. There are no specific limitations on the dicarboxylic acid to be used to form an ester structure, and examples thereof include reaction products between diols and phthalic acid, isophthalic acid, terephthalic acid, adipic acid, oxalic acid, maleic acid, fumaric acid, or sebacic acid. Of these, isophthalic acid and adipic acid are particularly preferable because they are relatively inexpensive, have high heat resistance, and maintain desirable compatibility with inks. Specific examples of the carbonate structure include pentamethylene carbonate diols, hexamethylene carbonate diols, hexane carbonate diols, and decane carbonate diols.

[0044] Good pigments include phthalocyanine based pigments, soluble azo pigments, insoluble azo pigments, lake pigments, quinacridone based pigments, isoindoline based pigments, indanthrene based pigments, metal complex based pigments, titanium oxide, zinc oxide, alumina white, calcium carbonate, barium sulfate, colcothar, cadmium red, chrome yellow, zinc yellow, Prussian blue, ultramarine blue, oxide coated glass powder, oxide coated mica, oxide coated metal particles, aluminum powder, gold powder, silver powder, copper powder, zinc powder, stainless steel powder, nickel powder, organic bentonite, iron oxide, carbon black, and graphite.

[0045] In addition, the ink may contain a photopolymerization initiator or other additives such as pigment dispersant, defoaming agent, and leveling agent. Although an ultraviolet curable ink can be used, it is preferable to use an ink that does not contain a photopolymerization initiator because it is not necessary to use a photopolymerization initiator when performing radiation curing. This is because decomposition products and unreacted components of a photopolymerization

initiator can cause problems such as odors and contamination of the contents.

[0046] As the printing machine to use for the method for producing printed matter according to the present invention, it is preferable to adopt a rotary press equipped with a center impression cylinder because it can serve to perform multicolor printing with high register accuracy even when using a thin plastic film as the base material and also serve to perform batch curing using a radiation source. Specifically, a good example is the CI-8 machine manufactured by COMEXI.

EXAMPLES

[0047] The invention is described specifically below with reference to examples. However, it should be noted that the present invention is not limited to these examples.

<Preparation of dampening solution>

[0048] Dampening solution 1: 90 parts by mass of pure water, 5 parts by mass of isopropanol, 4 parts by mass of propylene glycol monobutyl ether, 0.5 part by mass of Arabic gum, 0.2 part by mass of phosphoric acid, 0.2 part by mass of sodium phosphate, and 0.1 parts by mass of t-butyl hydroquinone were mixed to prepare 18 L of a dampening solution.

[0049] Dampening solution 2: Except for excluding t-butyl hydroquinone, the same preparation procedure as for the dampening solution 1 was carried out.

[0050] Dampening solution 3: Except for using 0.01 parts by mass of t-butyl hydroquinone, the same preparation procedure as for the dampening solution 1 was carried out.

[0051] To adjust the dissolved oxygen concentration at 15°C under 1 atm pressure, nitrogen bubbling was performed for reduction down to 3 ppm whereas an oxygen remover (dissolved oxygen remover machine manufactured by Kyowa Corporation) was used for reduction to a lower concentration. Adjustment of the dissolved oxygen concentration is performed by measuring it at appropriate times using a dissolved oxygen meter (DOM2000 manufactured by GS). It should be noted that adjustment of the dissolved oxygen concentration was not performed in Comparative example 2, whereas oxygen bubbling was performed to maintain the saturated oxygen concentration in Comparative Example 3.

<Preparation of active energy ray curable lithographic ink>

[0052] Ink 1: 30 parts by mass of Daiso DAP (registered trademark) K manufactured by Osaka Soda Co., Ltd., used as the resin having an ethylenically unsaturated group, 25 parts by mass of M600 manufactured by Miwon and 23 parts by mass of M3130 manufactured by Miwon, both used as polyfunctional (meth)acrylates, 18 parts by mass of Mogul E manufactured by Cabot, used as pigment black, 2 parts by mass of Micro Ace P-8 manufactured by Nippon Talc Co., Ltd., used as extender pigment, 1 part by mass of Disper BYK2013 manufactured by BYK, used as dispersing agent, and 1 part by mass of KTL-4N manufactured by Kitamura Limited, used as wax were kneaded in a three-roll mill to prepare an active energy ray curable lithographic ink.

[0053] Ink 2: 24 parts by mass of HIROS (registered trademark) VS-1259 manufactured by Seiko PMC Corporation, used as a resin free of an ethylenically unsaturated group, 34 parts by mass of M4004 manufactured by Miwon and 20 parts by mass of M262 manufactured by Miwon, both used as polyfunctional (meth)acrylates, 18 parts by mass of Mogul E manufactured by Cabot, used as pigment black, 2 parts by mass of Micro Ace P-8 manufactured by Nippon Talc Co., Ltd., used as extender pigment, 1 part by mass of Disper BYK2013 manufactured by BYK, used as dispersing agent, and 1 part by mass of KTL-4N manufactured by Kitamura Limited, used as wax were kneaded in a three-roll mill to prepare an active energy ray curable lithographic ink.

[0054] Ink 3: 28 parts by mass of Daiso DAP (registered trademark) K manufactured by Osaka Soda Co., Ltd., used as the resin having an ethylenically unsaturated group, 22 parts by mass of M600 manufactured by Miwon and 21 parts by mass of M3130 manufactured by Miwon, both used as polyfunctional (meth)acrylates, 8 parts by mass of Aronix (registered trademark) M-1200 manufactured by Toagosei Co., Ltd., used as urethane compound, 18 parts by mass of Mogul E manufactured by Cabot, used as pigment black, 2 parts by mass of Micro Ace P-8 manufactured by Nippon Talc Co., Ltd., used as extender pigment, 1 part by mass of Disper BYK2013 manufactured by BYK, used as dispersing agent, and 1 part by mass of KTL-4N manufactured by Kitamura Limited, used as wax were kneaded in a three-roll mill to prepare an active energy ray curable lithographic ink.

<Base material used>

[0055]

Base material 1 (PET): A film of PTM (manufactured by Unitika Ltd., thickness 12 μm) having a surface coated with

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polyester

Base material 2 (OPP): A film of P2111 (manufactured by Toyobo Co., Ltd., thickness 20 μm) having a surface treated with corona discharge

Base material 3 (polyamide): A film of ONM (manufactured by Unitika Ltd., thickness 15 μm) having a surface coated with polyurethane

Base material 4 (PET): A film of S-46 (manufactured by Polyplex, thickness 12 μm) having a surface coated with acrylic resin

Base material 5 (OPP): A film of P2002 (manufactured by Toyobo Co., Ltd., thickness 40 μm) having untreated surfaces

Base material 6 (polyvinyl alcohol): A film of Eval EF-XL (manufactured by Kuraray Co., Ltd., thickness 12 μm) having untreated surfaces

<Printing test>

[0056] A lithographic printing plate (XP-F, manufactured by FUJIFILM Corporation) was mounted on a lithographic printing machine for flexible packaging (CI-8, manufactured by Comexi) and various raw fabrics were printed at a rate of 150 m/min with an active energy ray curable lithographic ink using a dampening solution. Then, using an electron beam irradiation apparatus manufactured by E-beam, electron beam irradiation was performed at an acceleration voltage of 110 kV and an irradiation dose of 30 kGy to cure the active energy ray curable lithographic ink, thereby providing a printed sample.

<Measurement of adhesion strength>

[0057] A mixed laminating adhesive composed of Takelac A969V and Takenate A-5 (5:1 by mass), both manufactured by Mitsui Chemicals, Inc., was applied to the printed specimen prepared in the printing test to a thickness of 3.0 g/m² and laminated with an unstretched polypropylene film (CPP, P1128 manufactured by Toyobo Co., Ltd., thickness 30 μm). Subsequently, it was aged at 40°C for 3 days to provide a laminated sample. A strip with a width of 15 mm was cut out of a solid part, which had a 100% ink concentration, of the laminate sample and subjected to peeling test using a Tensilon universal testing machine (RTG-1210, manufactured by Orientec Corporation), in which peel strength was measured as peeling was performed at an angle of 90° at a rate of 300 mm/min. The sample was rated as good if showing a peel strength of 1 N/15 mm or more or rated as excellent if showing a peel strength of 3 N/15 mm or more or persistent until base material failure.

[Examples 1 to 5 and Comparative examples 1 to 3]

[0058] Lithographic printing of the base material 1 was performed using the ink 1 prepared above and the dampening solution 1 or dampening solution 2 specified in Table 1, each having a dissolved oxygen concentration, and results show that the adhesion strength tends to increase with a decreasing dissolved oxygen concentration in the dampening solution. The laminate peel strength exceeded 1 N/15 mm, proving high quality, at dissolved oxygen concentrations below 5 ppm. Results are given in Table 1.

[Table 1]

	Examples					Comparative examples		
	1	2	3	4	5	1	2	3
Type of dampening solution	1	1	1	2	2	1	1	1
Type of ink	1	1	1	1	1	1	1	1
Type of base material	1	1	1	1	1	1	1	1
Dissolved oxygen concentration in dampening solution (ppm)	4.5	3.0	0.5	4.6	0.5	5.8	7.5	10.7
Laminate peel strength (N/15 mm)	1.3	1.5	2.4	2.0	base material failure	0.8	0.4	0.2

[Examples 6 to 10]

[0059] Under the conditions in Example 3, printing was performed for each of the base materials 2 to 6 instead of the base material 1. Stronger adhesion tended to be achieved in films that underwent more intense generation of radicals on the outermost surface. Results are given in Table 2.

[Table 2]

	Examples				
	6	7	8	9	10
Type of dampening solution	1	1	1	1	1
Type of ink	1	1	1	1	1
Type of base material	2	3	4	5	6
Dissolved oxygen concentration in dampening solution (ppm)	0.4	0.5	0.5	0.4	0.4
Laminate peel strength (N/15 mm)	base material failure	4.2	base material failure	1.9	1.4

[Example 11]

[0060] Under the conditions in Example 3, printing was performed using the dampening solution 3 instead of the dampening solution 1. Results showed that a decrease in the antioxidant content in the dampening solution led to a slight increase in adhesion strength. Results are given in Table 3.

[Examples 12 and 13]

[0061] Under the conditions in Example 3, printing was performed using the ink 2 or the ink 3 instead of the ink 1. Results are given in Table 3.

[Table 3]

	Examples			
	3	11	12	13
Type of dampening solution	1	3	1	1
Type of ink	1	1	2	3
Type of base material	1	1	1	1
Dissolved oxygen concentration in dampening solution (ppm)	0.5	0.5	0.4	0.5
Laminate peel strength (N/15 mm)	2.4	2.6	1.8	3.9

INDUSTRIAL APPLICABILITY

[0062] The method for producing printed matter according to the present invention serves to achieve improved adhesion of an ink to a base material.

Claims

1. A method for producing printed matter using a lithographic printing plate **characterized in that** an active energy ray curable lithographic ink is transferred onto a base material and exposed to radiation and that a dampening solution having a dissolved oxygen concentration of 5 ppm or less is used.
2. A method for producing printed matter as set forth in claim 1, wherein the dampening solution is substantially free

of antioxidants.

3. A method for producing printed matter as set forth in either claim 1 or 2, wherein the radiation is an electron beam.

5 4. A method for producing printed matter as set forth in any one of claims 1 to 3, wherein the base material is a plastic film.

5. A method for producing printed matter as set forth in claim 4, wherein the plastic film contains a radiation crosslinkable polymer.

10 6. A method for producing printed matter as set forth in either claim 4 or 5, wherein the plastic film has an adhesive coated or a corona treated surface.

7. A method for producing printed matter as set forth in claim 6, wherein the adhesive coat is a polyurethane coat or an acrylic coat.

15 8. A method for producing printed matter as set forth in any one of claims 1 to 7, wherein the active energy ray curable lithographic ink contains a resin having an ethylenically unsaturated group.

20 9. A method for producing printed matter as set forth in any one of claims 1 to 8, wherein the active energy ray curable lithographic ink contains a urethane compound.

10. A method for producing printed matter as set forth in any one of claims 1 to 9, wherein a rotary printing press having a center impression cylinder is used.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/009369

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B41M1/06(2006.01)i, B41M1/30(2006.01)i, B41N3/08(2006.01)i
 FI: B41M1/06, B41M1/30Z, B41N3/08101

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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. B41M1/06, B41M1/30, B41N3/08

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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

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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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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-15755 A (TOYO INK MFG CO., LTD.) 20.01.2005 (2005-01-20), paragraphs [0065], [0066]	1-10
A	JP 2011-73193 A (FUJIFILM CORPORATION) 14.04.2011 (2011-04-14), paragraphs [0006], [0013]	1-10
A	JP 7-209880 A (DAINIPPON INK AND CHEMICALS INC.) 11.08.1995 (1995-08-11), claims 1, 3	1-10
A	JP 9-193490 A (TECNICAS ESPECIALES DE OXIGENACION SL) 29.07.1997 (1997-07-29), paragraph [0021]	1-10
A	EP 0876910 A1 (RUPRECHT HANDELS AG) 11.11.1998 (1998-11-11), column 1, lines 1-47	1-10

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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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Date of the actual completion of the international search
21.05.2020

Date of mailing of the international search report
02.06.2020

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/JP2020/009369
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JP 2011-73193 A	14.04.2011	(Family: none)
JP 7-209880 A	11.08.1995	(Family: none)
JP 9-193490 A	29.07.1997	US 5826514 A column 3, lines 21-43 US 6015140 A EP 770501 A2
EP 0876910 A1	11.11.1998	(Family: none)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004358788 A [0005]