



(11) **EP 2 492 338 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
29.08.2012 Bulletin 2012/35

(51) Int Cl.:
C11D 17/00 ^(2006.01) **C11D 3/04** ^(2006.01)
C11D 11/00 ^(2006.01)

(21) Application number: **12155725.0**

(22) Date of filing: **16.02.2012**

(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

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(30) Priority: **24.02.2011 JP 2011038351**

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(54) **Plate cleaning agent for lithographic printing plate and plate surface treatment method for lithographic printing plate**

(57) A plate cleaning agent is provided capable of suitably treating a plate surface without causing blinding in a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, and particularly an oxygen-blocking protective layer containing inorganic fine particles. The invention provides: an emulsified plate cleaning agent for a lithographic printing plate, which is used on a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, wherein the total cation content of a contained salt based on the total weight of

the plate cleaning agent is 0.5% by weight or more, and 30% by weight or more of the cations are at least one type selected from the group consisting of potassium, cesium and rubidium based on the weight of all cations; and a plate surface treatment method for a lithographic printing plate, this method comprising: cleaning a lithographic printing plate, obtained by platemasking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, with the above-mentioned emulsified plate cleaning agent for a lithographic printing plate.

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Description**BACKGROUND OF THE INVENTION**

Field of the Invention

[0001] The present invention relates to a plate cleaning agent for a lithographic printing plate, more particularly to an emulsified plate cleaning agent, and even more particularly to an emulsified plate cleaning agent used for a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer. In addition, the present invention relates to a plate surface treatment method for a lithographic printing plate that uses this emulsified plate cleaning agent.

Description of the Related Art

[0002] In general, lithographic printing plates typically comprise an oleophilic image area that is ink receptive during the printing process and a hydrophilic nonimage area that is fountain solution receptive during the printing process. Lithographic printing plates utilize the fact that water and oil of mutually repel to generate a difference in ink adherence to the surface of the lithographic printing plate by using the oleophilic image areas of the lithographic printing plate as ink receptive areas and the hydrophilic nonimage areas as a fountain solution receptive areas (areas not receptive to ink), thereby causing ink to only adhere to the image areas, followed by transferring the ink to a printed substrate such as paper. In lithographic printing, the nonimage areas are dampened with the fountain solution, the surface chemical difference between the image areas and the nonimage areas is enlarged, and ink repulsion between the nonimage areas and ink receptivity of the image areas are increased. Thus, if the hydrophilicity of the nonimage areas of a lithographic printing plate is impaired for some reason, ink frequently adheres to that region resulting in the occurrence of so-called "scumming", while conversely as a result of other components adhering to the image portion, the ink is unable to adhere thereto, thereby preventing an increase in the image density of the printed matter.

[0003] In the case hydrophilicity has been impaired and there is increased susceptibility to scumming, or in the case ink no longer adheres to the image areas, plate surface treatment is typically carried out on the lithographic printing plate using a plate cleaning agent in order to correct these problems and restore the hydrophilicity of the nonimage areas and the adherence of the image areas. In the past, various plate cleaning agents for lithographic printing plates have been proposed (see, for example, Japanese Patent Application Publication No. H11-288104 and Japanese Patent Application Publication No. 2007-45055).

[0004] On the other hand, from the viewpoint of lithographic printing plates, lithographic printing plate precursors (PS plates) have heretofore been widely used that are obtained by providing an oleophilic photosensitive resin (image recording layer) on a hydrophilic support. A lithographic printing plate is obtained by platemaking this type of lithographic printing plate precursor using a method consisting of exposing the lithographic printing plate precursor through an original image such as a lith film, followed by allowing the areas serving as the image areas of the image recording layer to remain while dissolving and removing other unwanted areas of the image recording layer with an alkaline developing solution or organic solvent to expose the surface of the hydrophilic support and form nonimage areas.

[0005] Digitization technology, consisting of electronically processing, accumulating and outputting image information with a computer, has become widespread in recent years, and various new image output methods have come to be used practically in accommodation of this digitization technology. Accompanying this, computer-to-plate (CTP) technology has attracted attention for use in directly producing lithographic printing plates without using a lith film by carrying digitized image information with highly convergent radiant rays of light in the manner of laser light, and exposing a lithographic printing plate precursor by scanning with the light.

[0006] Photopolymerizable lithographic printing plate precursors have been proposed as an example of a lithographic printing plate precursor for CTP as described above. Since a polymerization initiator (compound that initiates and promotes polymerization of a compound having polymerizable unsaturated groups by generating radicals with the energy of light, heat or both) is typically used in photopolymerizable lithographic printing plate precursors, an oxygen-blocking protective layer is normally provided on the image recording layer to improve polymerization efficiency by inhibiting the loss of radicals caused by oxygen in the air. Polyvinyl alcohol is a well-known example of a component of this protective layer. In addition, the containing of fine particles of inorganic substances in the oxygen-blocking protective layer has also been proposed (see, for example, Japanese Patent Application Publication No. 2005-119273).

[0007] Inorganic compounds used in this type of oxygen-blocking protective layer partially remain on the surface of the image areas after developing, and due to their own hydrophilicity and/or hydrophilic components in the foundation solution being adsorbed onto the surface of the inorganic compounds, adequate ink receptivity of the surface of the image areas is lost during printing, and as a result thereof, the problem of defective ink adherence occurs in which the ink concentration on printed matter decreases. The problem of ink failing to adhere to the image region during printing

is referred to as blinding. On the other hand, when scumming occurs during printing, there is the problem of increased likelihood of blinding when treatment is carried out with a plate cleaning agent, and so-called uneven wiping may occur when unevenness occurs in the adherence of ink as a result of treating with a plate cleaning agent.

[0008] With the foregoing in view, a plate cleaning agent is required that can be used favorably without causing problems such as blinding or uneven wiping on a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, and particularly an oxygen-blocking protective layer containing inorganic fine particles.

DISCLOSURE OF THE INVENTION

Problem to be solved by the Invention

[0009] An object of the present invention is to provide a plate cleaning agent capable of favorably treating a plate surface without causing blinding in a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, and particularly an oxygen-blocking protective layer containing inorganic fine particles.

Means to Solve the Problem

[0010] As a result of conducting extensive studies to achieve the above object, the inventors of the present invention found that the type and amount of cation in a plate cleaning agent is involved in the occurrence of blinding, and accordingly, plate cleaning treatment can be favorably carried out while inhibiting the occurrence of blinding without causing uneven adherence of ink in an image areas by selecting a specific mode for the cation in the plate cleaning agent, thereby leading to completion of the present invention.

[0011] Thus, the present invention is an emulsified plate cleaning agent for a lithographic printing plate used on a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, wherein the total cation content of a contained salt based on the total weight of the plate cleaning agent is 0.5% by weight or more, and 30% by weight or more of the cations are at least one type selected from the group consisting of potassium, cesium and rubidium based on the weight of all cations. Here, a salt includes salts in the manner of organic salts and inorganic salts, as well as hydroxides.

[0012] In a preferred embodiment of the present invention, the emulsified plate cleaning agent for a lithographic printing plate is used in a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor in which the oxygen-blocking protective layer contains inorganic fine particles.

[0013] Moreover, the present invention is directed to a plate surface treatment method for a lithographic printing plate that comprises cleaning a lithographic printing plate, obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, with the above-mentioned emulsified plate cleaning agent for a lithographic printing plate. In particular, the plate surface treatment method of the present invention is suitable for treating a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer containing inorganic fine particles.

Effect of the Invention

[0014] According to the emulsified plate cleaning agent of the present invention, scum removal ability is demonstrated against various types of scumming in nonimage areas and defective ink adherence and uneven wiping are prevented from occurring in image areas in a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer.

[0015] According to the emulsified plate cleaning agent of the present invention, high-quality printed matter can be provided by carrying out favorable plate cleaning treatment on a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, and particularly an oxygen-blocking protective layer containing inorganic fine particles.

Mode for Carrying Out the Invention

[0016] A salt that provides a cation is contained as a component thereof in the emulsified plate cleaning agent for a lithographic printing plate of the present invention. Salts in the manner of organic salts and inorganic salts as well as hydroxides and the like are included in the salt that provides a cation used in the present invention, and any of normal salts, acid salt, basic salts, double salts or complex salts and the like are included. The salt that provides a cation used in the present invention can be selected from known salts and hydroxides for use as a component in the plate cleaning

agent for a lithographic printing plate. The emulsified plate cleaning agent for a lithographic printing plate of the present invention is required to contain at least one type of cation originating in the above-mentioned salt selected from potassium (K), cesium (Cs) and rubidium (Rb). Namely, the emulsified plate cleaning agent for a lithographic printing plate of the present invention is required to contain a salt that provides at least one type of cation at least selected from the group consisting of potassium, cesium and rubidium. Furthermore, a cation originating in a salt contained in the emulsified plate cleaning agent for a lithographic printing plate of the present invention does not include a cation originating in the water used to prepare the plate cleaning agent.

[0017] The content of all cations originating in the contained salt of the emulsified plate cleaning agent for a lithographic printing plate of the present invention is 0.5% by weight or more, preferably 1.0% by weight or more and typically 10% by weight or less based on the total weight thereof, and 30% by weight or more of the cations are at least one type of cation selected from the group consisting of potassium, cesium and rubidium based on the weight of all cations.

[0018] All cations originating in the salt contained in the emulsified plate cleaning agent for a lithographic printing plate of the present invention may be at least one type of cation selected from the group consisting of potassium, cesium and rubidium.

[0019] As an example of the composition thereof, the emulsified plate cleaning agent for a lithographic printing plate of the present invention can be composed of an aqueous phase containing (1) a water-soluble polymer compound, (2) at least one type of compound selected from the group consisting of phosphoric acid, polyphosphoric acid and salts thereof such as alkaline metal salts, organic phosphonic acid and salts thereof, (3) nitric acid and/or nitrates, (4) sulfuric acid, sulfates and/or bisulfates, (5) water, and an oily phase containing (6) a hydrocarbon-based solvent having a dissolving action on ink. The emulsified plate cleaning agent for a lithographic printing plate of the present invention can also contain (7) a surfactant, (8) a wetting agent, (9) a thixotropic agent, and (10) a pH adjuster as necessary. A preservative, disinfectant or colorant and the like may also be added to the plate cleaning agent of the present invention in addition to the above-mentioned components.

[0020] Specific examples of the water-soluble polymer compound of (1) include natural substances and their modified forms, such as dextrin, cyclodextrin, alginates, fibrin derivatives (such as carboxymethyl cellulose, carboxyethyl cellulose, hydroxyethyl cellulose and methyl cellulose), gum arabic or soybean polysaccharides, and synthetic products such as polyvinyl alcohol and derivatives thereof, polyvinylpyrrolidone, polyacrylamide and copolymers thereof, acrylic acid copolymers, vinyl methyl ether/maleic anhydride copolymers, vinyl acetate/maleic anhydride copolymers or styrene/maleic anhydride copolymers.

[0021] Examples of polysaccharides extracted from soybeans that have the ability to form a film include water-soluble soybean polysaccharides. Water-soluble soybean polysaccharides contain constituent sugars such as rhamnose, fucose, arabinose, xylose, galactose, glucose or uronic acid, and the average molecular weight thereof is 50,000 to 1,000,000. The content of water-soluble soybean polysaccharide in the plate cleaning agent of the present invention is suitably within the range of 0.5% by weight to 20% by weight and preferably 1% by weight to 10% by weight. The water-soluble soybean polysaccharide is used in the form of a homogeneous aqueous solution by dissolving in water or warm water at 50°C or lower. A production method for this type of water-soluble soybean polysaccharide is described in Japanese Patent Application Publication No. H5-32701. In addition, an example of a commercially available product of the water-soluble soybean polysaccharide is Soyafib-S-LN (Fuji Oil Co., Ltd.) and the like. A soybean polysaccharide having a viscosity of a 10% by weight aqueous solution thereof (25°C) within the range of 5 cp to 100 cp is preferably used as a water-soluble soybean polysaccharide able to be used in the present invention.

[0022] These substances can be used alone or as a mixture, and in order to allow the plate cleaning agent to have a preferable viscosity range (about 100 cps to 1000 cps), their amount used is suitably 1% by weight to 24% by weight, and can be more preferably selected from the range of 3% by weight to 20% by weight based on the total weight of the plate cleaning agent.

[0023] Examples of the component (2) include phosphoric acid, sodium phosphate, potassium phosphate, lithium phosphate, pyrophosphoric acid, sodium pyrophosphate, potassium pyrophosphate, lithium pyrophosphate, triphosphoric acid, sodium triphosphate, potassium triphosphate, lithium triphosphate, tetraphosphoric acid, sodium tetraphosphate, potassium tetraphosphate, lithium tetraphosphate, metaphosphoric acid, sodium metaphosphate, potassium metaphosphate, lithium metaphosphate, trimetaphosphoric acid, sodium trimetaphosphate, potassium trimetaphosphate, lithium trimetaphosphate, hexametaphosphoric acid, sodium hexametaphosphate, potassium hexametaphosphate, lithium hexametaphosphate, methylene diphosphonic acid, 1-hydroxyethane-1,1-disulfonic acid, nitrilotrisphosphonic acid, N-carboxymethyl-N,N-di(methylenephosphonic acid), hexamethylenediamine-tetra(methylenephosphonic acid), ethylenediamine-tetra(methylenephosphonic acid) diethylenetriamine-penta(methylenephosphonic acid), N,N-di(carboxymethyl)-N-methylenephosphonic acid, N-(2-hydroxyethyl)-N,N-di(methylenephosphonic acid), N-hydroxymethyl-N,N',N'-ethylenediaminetris(methylenephosphonic acid), N-hydroxyethyl-N',N'-diethylethylenediamine-N,N,N',N'-tetra(methylenephosphonic acid), di(2-hydroxypropylene)triamine penta(methylenephosphonic acid), and tri(2-hydroxypropylene)tetraaminehexa(methylenephosphonic acid) and the like. These compounds can also be acquired as commercially available products, and are commercially available as, for example, the Dequest series available from Monsanto

Chemical Company or the Wayplex series available from the Wayland Chemical Division of the Philip A. Hant Chemical Corp. The above-mentioned compounds can be used alone or two or more types can be used in combination, and are contained within the range of 0.1% by weight to 15% by weight and more preferably within the range of 0.5% by weight to 10% by weight based on the total weight of the plate cleaning agent according to the present invention.

[0024] Examples of the nitric acid and/or nitrates of component (3) used in the present invention include, in addition to nitric acid, nitrates in the form of metal salts of nitric acid, in the manner of zinc nitrate, cobalt nitrate, magnesium nitrate, sodium nitrate, potassium nitrate, nickel nitrate, bismuth nitrate, tin nitrate, strontium nitrate, cesium nitrate, rubidium nitrate and cerium nitrate, as well as ammonium nitrate. The usage range of the nitric acid and/or water-soluble nitric acid metal salt used in the present invention is 0.1% by weight to 10% by weight, and more preferably 0.5% by weight to 5% by weight, based on the total weight of the plate cleaning agent.

[0025] Examples of the sulfuric acid, sulfates and/or bisulfates of component (4) used in the present invention include, in addition to sulfuric acid, sulfates or bisulfates such as sodium sulfate, potassium sulfate, cesium sulfate, rubidium sulfate or aluminum sulfate. Bisulfates are represented by the general formula $M(HSO_4)_n$ (wherein, M represents a metal and n indicates the valence of M), and examples thereof include strontium bisulfate, potassium bisulfate, calcium bisulfate, thallium bisulfate, sodium bisulfate, lead bisulfate, bismuth bisulfate, magnesium bisulfate and rhodium bisulfate. These compounds can be used alone or two or more types can be used in combination, and are contained within a range of 0.01% by weight to 5% by weight, and more preferably 0.1% by weight to 3% by weight, based on the total weight of the plate cleaning agent according to the present invention.

[0026] Although the remaining component of the aqueous phase of the plate cleaning agent of the present invention is water, the amount thereof is suitably 45% by weight to 85% by weight, and more preferably 50% by weight to 80% by weight, based on the total weight of the plate cleaning agent of the present invention.

[0027] On the other hand, the hydrocarbon-based solvent of component (6) can be used concurrently in the oily phase of the plate cleaning agent of the present invention. A petroleum residue normally used to clean printing ink having a boiling point of 120°C to 350°C is particularly useful for use as the component (6). Specific examples of such hydrocarbon-based solvents include products manufactured by Nippon Petrochemicals Co., Ltd. consisting of Cleansol (volatile oil), dry solvent, A solvent, K solvent, mineral spirit A and Hiarom 25 having melting points of 150°C to 200°C, insecticide solvent, fog solvent and non-sulfur solvent having boiling points of 200°C to 250°C, and no. 3 solvent, no. 4 solvent, no. 5 solvent, no. 6 solvent and no. 7 solvent having boiling points of 250°C to 300°C, as well as tall oil fatty acid ester, Swasol (aromatic-based, high boiling point solvent, Maruzen Petrochemical Co., Ltd.), Exxsol (Exxon Chemical Japan, Ltd.) and Exxol (naphthalene-based solvent, ExxonMobil Corp.). The usage range of these hydrocarbon-based solvents is suitably 1% by weight to 50% by weight, and more preferably 5% by weight to 35% by weight, based on the total weight of the plate cleaning agent.

[0028] Since component (6) is not miscible with the water of component (5), it is used in an adequately mixed and dispersed state at the time of use. It is useful to add the surfactant of component (7) for the purpose of enhancing dispersion stability at this time. Surfactants able to be used in the present invention consist of anionic surfactants and nonionic surfactants.

[0029] Examples of anionic surfactants include fatty acid salts, abietic acid salts, hydroxyalkanesulfonic acid salts, alkanesulfonic acid salts, dialkylsulfosuccinic acid salts, linear alkylbenzenesulfonic acid salts, branched alkylbenzenesulfonic acid salts, alkylnaphthalenesulfonic acid salts, alkylphenoxypolyoxyethylene propylsulfonic acid salts, polyoxyethylene alkyl sulfophenyl ether salts, sodium N-methyl-N-oleytaurate, disodium N-alkylsulfosuccinate monoamide, petroleum sulfonic acid salts, sulfated castor oil, sulfated beef tallow, sulfuric acid ester salts of fatty acid alkyl esters, alkyl sulfate ester salts, polyoxyethylene alkyl ether sulfate ester salts, fatty acid monoglyceride sulfate ester salts, polyoxyethylene alkyl phenyl ether sulfate ester salts, polyoxyethylene styryl phenyl ether sulfate ester salts, alkyl phosphate ester salts, polyoxyethylene alkyl ether phosphate ester salts, polyoxyethylene alkyl phenyl ether phosphate ester salts, partially saponified styrene-maleic anhydride copolymers, partially saponified olefin-maleic anhydride copolymers, naphthalene sulfonate formalin condensates and the like. Among these, dialkylsulfosuccinic acid salts, alkyl sulfate esters and alkylbenzenesulfonic acid salts are used particularly preferably.

[0030] In addition, examples of nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene polystyryl phenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, glycerin fatty acid partial esters, sorbitan fatty acid partial esters, pentaerythritol fatty acid partial esters, propylene glycol mono fatty acid esters, sucrose fatty acid partial esters, polyoxyethylene sorbitan fatty acid partial esters, polyoxyethylene sorbitol fatty acid partial esters, polyethylene glycol fatty acid esters, polyglycerin fatty acid partial esters, polyoxyethylated castor oil, polyoxyethylene glycerin fatty acid partial esters, fatty acid diethanolamides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamines, triethanolamine fatty acid esters, trialkylamine oxides and the like. Among these, sorbitan fatty acid partial esters, polyoxyethylated castor oil ethers, polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers and polyoxyethylene-polyoxypropylene block polymers are used preferably. Two or more types of these surfactants may be used concurrently. Although there are no particular limitations on the amount of surfactant used, a preferable range is 0.5% by weight to 10% by weight based on the total weight of the plate cleaning agent.

[0031] In addition to the above-mentioned components, one type or two or more types of wetting agents (component (8)) are useful for imparting favorable spreading characteristics to the plate cleaning agent, suppressing drying and imparting favorable usage appropriateness. Suitable wetting agents are compounds represented by the general formula: $\text{HO}-(\text{R}-\text{O})_n-\text{H}$ (wherein, R represents C_mH_{2m} ($m = 2$ to 6), and n represents 1 to 500). Specific examples of preferable compounds include ethylene glycol, propylene glycol, butylene glycol, pentanediol, hexylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol and tripropylene glycol, while glycerin, sorbitol and pentaerythritol are useful as other wetting agents. The amount of wetting agent used is typically within the range of 0.5% by weight to 10% by weight, and more preferably within the range of 1% by weight to 5% by weight, based on the total weight of the plate cleaning agent.

[0032] The thixotropic agent of component (9) improves work properties when treating a plate surface with a sponge and the like by lowering viscosity of the liquid with dynamic pressure and raising viscosity when still. Examples of suitable thixotropic agents include finely powdered silicic acid, pumice, calcium carbonate, zeolite and the like. The amount used is suitably within the range of 0.5% by weight to 10% by weight, and preferably within the range of 1% by weight to 7% by weight, based on the total weight of the plate cleaning agent.

[0033] The plate cleaning agent of the present invention is preferably adjusted to be acidic, and more specifically, to a pH range of 1.0 to 4.0 , preferably to a pH range of 1.5 to 4.0 , and more preferably to a pH range of 1.5 to 3.0 . A pH adjuster (component (10)) can be used to adjust to these pH ranges. Examples of pH adjusters that can be used include phosphoric acid, nitric acid, sulfuric acid, phosphorous acid and organic carboxylic acids such as citric acid, acetic acid, malonic acid, tartaric acid, malic acid, lactic acid, levulinic acid, butyric acid, maleic acid or picolinic acid. In addition, bases in the form of metal hydroxides such as hydroxides of alkaline metals or alkaline earth metals may also be used concurrently. Examples of such metal hydroxides include sodium hydroxide, potassium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, beryllium hydroxide, magnesium hydroxide, calcium hydroxide and barium hydroxide.

[0034] In addition to the above-mentioned components, preservatives (disinfectants), colorants and the like can also be added. Examples of preservatives include phenol or derivatives thereof, formalin, imidazole derivatives, sodium dihydroacetate, 4-isothiazolin-3-one derivatives, benzisothiazolin-3-one derivatives, benzotriazole derivatives, amidine-guanidine derivatives, pyridine quaternary ammonium salts, quinoline-guanidine derivatives, diazine, triazole derivatives, oxazole, oxazine derivatives and bromonitroalcohol-based preservatives such as 2-bromo-2-nitropropane-1,3-diol. The preferable amount of preservative added is an amount that stably demonstrates efficacy against bacteria, molds, yeast and the like, is typically added at roughly 0.01% by weight to 3% by weight based on the total weight of the plate cleaning agent, and two or more types of preservatives are preferably used concurrently so as to be effective against various molds and bacteria. The colorant is used to impart visual contrast by imparting a desired color tone to the plate cleaning agent of the present invention, and can be selected from a wide range of dyes. Particularly preferable examples of colorants used include blue, violet and red colorants. Specific examples include crystal violet, safranin, brilliant blue, malachite green and acid rhodamine B. The amount used is suitably 0.0001% by weight to 0.1% by weight, and more preferably within the range of 0.0003% by weight to 0.05% by weight, based on the total weight of the plate cleaning agent.

[0035] The emulsified plate cleaning agent for a lithographic printing plate of the present invention can be produced in accordance with ordinary methods as a typical emulsified O/W type or W/O type of emulsion.

[0036] The emulsified plate cleaning agent for a lithographic printing plate of the present invention can be preferably used for a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate in which is provided an oxygen-blocking protective layer, and particularly an oxygen-blocking protective layer containing inorganic fine particles. An example of such a photopolymerizable lithographic printing plate precursor is described in Japanese Patent Application Publication No. 2005-119273.

[0037] The structure of a photopolymerizable lithographic printing plate precursor able to be preferably used by the plate cleaning agent of the present invention is that of a lithographic printing plate precursor having an image recording layer containing (A) an active light absorber, (B) a polymerization initiator and (C) a polymerizable compound, and an oxygen-blocking protective layer containing inorganic fine particles, and particularly inorganic layered compounds, in that order.

[0038] The following provides a brief explanation of the configuration of the above-mentioned photopolymerizable lithographic printing plate precursor, platemaking process and printing process.

[Oxygen-Blocking Protective Layer]

[0039] Inorganic fine particles contained in the oxygen-blocking protective layer are classified into spherical fine particles and layered fine particles.

[Spherical Fine Particles]

[0040] Examples of inorganic spherical fine particles include those of metals and metal compounds such as oxides, composite oxides, hydroxides, carbonates, sulfates, silicates, phosphates, nitrides, carbides, sulfides and composite compounds of at least two or more types thereof, and more specifically, glass, zinc oxide, silica, alumina, zircon oxide, tin oxide, potassium titanate, strontium titanate, aluminum borate, magnesium oxide, magnesium borate, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, titanium hydroxide, basic magnesium sulfate, calcium carbonate, magnesium carbonate, calcium sulfate, magnesium sulfate, calcium silicate, magnesium silicate, calcium phosphate, silicon nitride, titanium nitride, aluminum nitride, silicon carbide, titanium carbide, zinc sulfide and composite compounds of at least two or more types thereof. Preferable examples include glass, silica, alumina, potassium titanate, strontium titanate, aluminum borate, magnesium oxide, calcium carbonate, magnesium carbonate, calcium silicate, magnesium silicate, calcium phosphate and calcium sulfate.

[0041] Preferable examples of silica fine particles include Snowtex 50 (particle size: 0.025 μm), Snowtex O-40 (particle size: 0.025 μm), Snowtex CM (particle size: 0.025 μm), Snowtex 20L (particle size: 0.045 μm), Snowtex XL (particle size: 0.05 μm), Snowtex YL (particle size: 0.65 μm), Snowtex ZL (particle size: 0.85 μm), MP1040 (particle size: 0.1 μm), MP2040 (particle size: 0.2 μm), MP3040 (particle size: 0.3 μm), MP1040 (particle size: 0.1 μm) and MP4540M (particle size: 0.45 μm) manufactured by Nissan Chemical Industries, Ltd., and Sylsya 310 (particle size: 1.4 μm), Sylsya 320 (particle size: 1.6 μm), Sylsya 350 (particle size: 1.8 μm), Sylsya 370 (particle size: 3.0 μm), Sylsya 530 (particle size: 1.9 μm), Sylsya 550 (particle size: 2.7 μm), Sylsya 250 (particle size: 2.7 μm) and Sylsya 430 (particle size: 2.5 μm) manufactured by Fuji Silysia Chemical Ltd.

[0042] Inorganic-organic composite fine particles are also preferable, and preferable examples thereof include synthetic resin particles and natural polymer particles, preferably resin particles such as those of acrylic resin, polyethylene, polypropylene, polyethylene oxide, polypropylene oxide, polyethyleneimine, polystyrene, polyurethane, polyurea, polyester, polyamide, polyimide, carboxymethyl cellulose, gelatin, starch, chitin, chitosan and the like, and more preferably composite fine particles in which the surface of resin particles such as those of acrylic resin, polyethylene, polypropylene or polystyrene is coated with the above-mentioned inorganic fine particles.

[0043] Among these inorganic spherical fine particles, those in which the inorganic component is silica (SiO_2) are particularly preferable from the viewpoints of dispersion stability when using as a coating solution, cost and high coefficient of friction.

[0044] The size of the inorganic spherical fine particles is such that the average particle size is preferably 0.001 μm to 1 μm , more preferably 0.03 μm to 0.5 μm , and even more preferably 0.05 μm to 0.2 μm . If the particle size is excessively large, image formation sensitivity decreases to a considerable decrease in oxygen blocking, and due to the smaller contact area of the organic fine particles, the effect of increasing the coefficient of friction is insufficiently obtained resulting in increased susceptibility to shifting. If the particle size is excessively small, the structure of the inorganic layered compounds is unable to be disrupted, preventing obtaining of the effect of inhibiting fogging. Adequate effects with respect to coefficient of friction are unable to be obtained relative to the amount of spherical fine particles added due to a decrease in the amount of protrusions from the surface, thereby resulting in the problem of a lack of balance with image forming performance.

[0045] The above-mentioned average particle size is measured with the centrifugal sedimentation method using a particle size distribution measuring device (BI-DCP, Brookhaven Instruments).

[0046] The content of the total inorganic spherical fine particle component contained in the protective layer is preferably 0.1% by weight to 80% by weight, more preferably 1% by weight to 50% by weight, and even more preferably 5% by weight to 30% by weight.

[Inorganic Layered Fine Particles]

[0047] Examples of inorganic layered fine particles include particles in the form of thin plates, including those belonging to the mica group such as natural mica or synthetic mica represented by the following general formula: $\text{A}(\text{B,C})_{2-5}\text{D}_4\text{O}_{10}(\text{OH,F,O})_2$ (wherein, A represents K, Na or Ca, B and C represent Fe(II), Fe(III), Mn, Al, Mg or V, and D represents Si or Al), and talc represented by the formula: $3\text{MgO} \cdot 4\text{SiO} \cdot \text{H}_2\text{O}$, taeniolite, montmorillonite, saponite, hectorite and zirconium phosphate.

[0048] Examples of natural mica belonging to the above-mentioned mica group include muscovite, paragonite, phlogopite, biotite and lepidolite. In addition, examples of synthetic mica include non-swellable mica such as fluor-phlogopite $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\text{F}_2$ or potassium tetrasilicate mica $\text{KMg}_{2.5}(\text{Si}_4\text{O}_{10})\text{F}_2$, and swellable mica such as Na tetrasilicate mica $\text{NaMg}_{2.5}(\text{Si}_4\text{O}_{10})\text{F}_2$, Na or Li taeniolite $(\text{Na,Li})\text{Mg}_2\text{Li}(\text{Si}_4\text{O}_{10})\text{F}_2$, or montmorillonite-based Na or Li hectorite $(\text{Na,Li})_{1/8}\text{Mg}_{2/5}\text{Li}_{1/8}(\text{Si}_4\text{O}_{10})\text{F}_2$. Moreover, synthetic smectite is also useful.

[0049] Among the above-mentioned inorganic layered compounds, synthetic inorganic layered compounds in the form of fluorine-based swellable micas are particularly useful. Namely, the swellable synthetic micas and swellable clay

minerals such as montmorillonite, saponite, hectorite, bentonite and the like have a layered structure composed of unit crystal lattice layers having a thickness of about 10 Å to 15 Å, and metal atom substitution within the lattice is considerably greater than other clay minerals. As a result, a positive charge deficiency occurs in the lattice layers, and in order to compensate for this, cations such as Na⁺, Ca²⁺ or Mg²⁺ are adsorbed between the layers. These cations interposed between the layers are referred to as exchangeable cations, and are exchanged with various cations. In the case the interlayer cations are Li⁺ or Na⁺ in particular, bonding between the layered crystal lattices is weak due to the small ionic radius thereof, causing these layered compounds to be swelled considerably by water. When shear is applied while in this state, cleavage occurs readily and a stable sol is formed in water. Bentonite and swellable synthetic micas strongly demonstrate this tendency making them more useful, and swellable synthetic micas are used particularly preferably.

[0050] From the viewpoint of controlling diffusion, the shape of the inorganic layered compounds used is such that the thickness is as thin as possible, and the size of the flat side is preferably as large as possible provided smoothness of the coated surface and transmission of active light are not impaired. Thus, the aspect ratio is 20 or more, preferably 100 or more and particularly preferably 200 or more. Furthermore, aspect ratio represents the ratio of diameter to thickness of the particles, and can be measured from, for example, a projection of the particles obtained from a micrograph.

Greater effects are obtained the larger the aspect ratio.

[0051] The particle size of the organic layered compounds used is such that the average diameter is 0.3 μm to 20 μm, preferably 0.5 μm to 10 μm and particularly preferably 1 μm to 5 μm. In addition, the average thickness of the particles is 0.1 μm or less, preferably 0.05 μm or less and particularly preferably 0.01 μm or less. For example, among the inorganic layered compounds, the size of a typical compound in the form of swellable synthetic mica is such that the thickness is 1 nm to 50 nm and the face size is about 1 μm to 20 μm.

[0052] If particles of an inorganic layered compound having a large aspect ratio in this manner are contained in the oxygen-blocking protective layer, coated film strength improves, and since the permeation of oxygen and moisture can be effectively prevented, deterioration of the oxygen-blocking protective layer caused by deformation and the like is prevented, and even if stored for a long period of time under conditions of high humidity, storage stability is superior without demonstrating decreases in image forming performance in the lithographic printing plate precursor caused by changes in humidity.

[0053] The content of the inorganic layered compound in the protective layer is preferably at weight ratio of 5/1 to 1/100 based on the amount of binder used in the protective layer. In the case of combining the use of several types of inorganic layered compounds, the total amount of these inorganic layered compounds is preferably within the range of the above-mentioned weight ratio.

[0054] A binder is preferably used in the oxygen-blocking protective layer along with the above-mentioned inorganic fine particles.

[0055] There are no particular limitations on the binder provided it facilitates dispersibility of inorganic fine particles such as layered fine particles and enables the formation of a uniform film that adheres to the image recording layer, and both water-soluble polymers and water-insoluble polymers can be suitably selected and used. Specific examples include water-soluble polymers such as polyvinyl alcohol, modified polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl imidazole, polyacrylic acid, polyacrylamide, partially saponified polyvinyl acetate, ethylene-vinyl alcohol copolymer, water-soluble cellulose derivatives, gelatin, starch derivatives, gum arabic and the like, and polymers such as polyvinylidene chloride, poly(meth)acrylonitrile, polysulfone, polyvinyl chloride, polyethylene, polycarbonate, polystyrene, polyamide, cellophane and the like. Two or more types of these can also be used in combination as necessary.

[0056] Among these, water-soluble polymers are preferable from the viewpoints of ease of removal of the protective layer remaining on nonimage areas and handling ease during film formation, with polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl imidazole, water-soluble acrylic resins such as polyacrylic acid, gelatin, gum arabic and the like being preferable, and in particular, polyvinyl alcohol, polyvinylpyrrolidone, gelatin and gum arabic being more preferable from the viewpoints of being able to be coated using water as a solvent and being easily removed by fountain solution during printing.

[0057] A portion of the polyvinyl alcohol able to be used in the oxygen-blocking protective layer may be substituted with an ester, ether or acetal provided a substantial amount of unsubstituted vinyl alcohol units having the required water solubility are contained. In addition, a portion may similarly contain other polymer components. Specific examples of polyvinyl alcohols include those of which 71 mol% to 100 mol% are hydrolyzed that have a degree of polymerization within the range of 300 to 2400. More specifically, examples of these include PVA-105, PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA-124H, PVA-CS, PVA-CST, PVA-HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613 and L-8 manufactured by Kuraray Co., Ltd. Examples of the above-mentioned copolymers include polyvinyl acetate chloroacetate or propionate, polyvinylformal, polyvinylacetal and copolymers thereof of which 88 mol% to 100 mol% are hydrolyzed.

[0058] The above-mentioned inorganic fine particles, such as layered fine particles, are dispersed in water by a suitable method followed by the preparation of an oxygen-blocking protective layer coating liquid from this dispersion. Known additives such as surfactants for improving coatability or water-soluble plasticizers for improving physical properties of the film can be added to the oxygen-blocking protective layer coating liquid in addition to the above-mentioned compo-

nents. The prepared oxygen-blocking protective layer coating liquid is coated onto an image recording layer provided on a support followed by drying to form the oxygen-blocking protective layer. Although the coating solvent can be suitably selected in correlation with the binder, in the case of using a water-soluble polymer, it is preferable use distilled water or purified water. There are no particular limitations on the method used to coat the oxygen-blocking protective layer, and a known method can be applied, such as that described in U.S. Patent No. 3,458,311 or that described in Japanese Examined Patent Application Publication No. S55-49729. More specifically, examples of methods used to coat the oxygen-blocking protective layer include blade coating, air knife coating, gravure coating, roll coating, spray coating, dip coating, bar coating and the like.

[0059] The coated amount of the oxygen-blocking protective layer in terms of the coated amount after drying is preferably within the range of 0.01 g/m² to 10 g/m², more preferably within the range of 0.02 g/m² to 3 g/m², and most preferably within the range of 0.02 g/m² to 1 g/m².

Components Comprising Image Recording Layer

[(A) Active Light Absorber]

[0060] The active light absorber is a compound that absorbs light radiated by a exposure light source, efficiently generates radicals from the polymerization initiator in a photon mode and/or heat mode, and contributes to improving the sensitivity of the lithographic printing plate precursor. The active light absorber is preferably an infrared absorber in the case of imagewise exposure of the lithographic printing plate precursor with an infrared laser, while a sensitizing dye that absorbs light of a wavelength of 250 nm to 420 nm is preferable in the case of imagewise exposure of the lithographic printing plate precursor with an ultraviolet laser for images. The infrared absorber is preferably a dye or pigment that has an absorption maximum at a wavelength of 760 nm to 1200 nm. A known infrared absorber can be suitably selected for this infrared absorber.

[0061] Particularly preferable examples of these dyes include cyanine dyes, squarylium dyes, pyrylium salts, nickel thiolate complexes and indolenine cyanine dyes. Cyanine dyes and indolenine cyanine dyes are more preferable.

[0062] These infrared absorbers can be added at a ratio of 0.001% by weight to 50% by weight, preferably 0.005% by weight to 30% by weight, and particularly preferably 0.01% by weight to 10% by weight based on the total solid fraction of the image recording layer. If within these ranges, high sensitivity is obtained without having an undesirable effect on uniformity or film strength of the image recording layer.

[0063] In addition, a sensitizing dye may also be used, and the sensitizing dye used is a compound having absorption at a wavelength of 250 nm to 420 nm, specific examples of which include benzoin, benzoin methyl ether, benzoin ethyl ether, 9-fluorenone, 2-chloro-9-fluorenone, 2-methyl-9-fluorenone, 9-anthrone, 2-bromo-9-anthrone, 2-ethyl-9-anthrone, 9,10-anthraquinone, 2-ethyl-9,10-anthraquinone, 2-t-butyl-9,10-anthraquinone, 2,6-dichloro-9,10-anthraquinone, xanthone, 2-methylxanthone, 2-methoxyxanthone, thioxanthone, benzyl, dibenzalacetone, p-(dimethylamino)phenyl styryl ketone, p-(dimethylamino)phenyl p-methyl styryl ketone, benzophenone, p-(dimethylamino) benzophenone (or Michler's ketone), p-(diethylamino) benzophenone and benzanthrone.

[0064] These sensitizing dyes can be added preferably at a ratio of 0.1% by weight to 50% by weight, more preferably 0.5% by weight to 30% by weight and particularly preferably 0.8% by weight to 20% by weight based on the total solid fraction that composes the image recording layer.

[(B) Polymerization Initiator]

[0065] The polymerization initiator is a compound that initiates and promotes the polymerization of a compound having polymerizable unsaturated groups by generating radicals using light energy, heat energy or both. Examples of polymerization initiators that can be used include known thermal polymerization initiators, compounds having bonds with weak bond dissociation energy, and photopolymerization initiators.

[0066] Examples of the polymerization initiators as described above include organic halogen compounds, carbonyl compounds, organic peroxides, azo-type polymerization initiators, azide compounds, metallocene compounds, hexarylbiimidazole compounds, organic boron compounds, disulfone compounds, oxime ester compounds, oxime ether compounds and onium salt compounds.

[0067] The polymerization initiator used preferably has a maximum absorption wavelength of 400 nm or less, more preferably a maximum absorption wavelength of 360 nm or less, and most preferably a maximum absorption wavelength of 300 nm or less. The incandescent stability of the lithographic printing plate precursor is improved by using an absorption wavelength for the ultraviolet range in this manner.

[0068] These polymerization initiators can be added at a ratio 0.1% by weight to 50% by weight, preferably 0.5% by weight to 30% by weight and particularly preferably 1% by weight to 20% by weight based on the total solid fraction composing the image recording layer. If within these ranges, favorable sensitivity and favorable resistance to scumming

of nonimage areas during printing can be obtained. Only one type of these polymerization initiators may be used or two or more types may be used in combination. In addition, these polymerization initiators may be added to the same layer with other components, or a separate layer may be provided followed by adding the polymerization initiators thereto.

5 [(C) Polymerizable Compound]

[0069] The polymerizable compound used in the image recording layer is an addition polymerizable compound that has at least one ethylenically unsaturated double bond, and is selected from compounds having at least one, and preferably two, terminal ethylenically unsaturated bonds. Such groups of compounds are widely known in the pertinent industrial field, and can be used without any particular limitations thereon. These compounds have a chemical form of, for example, a monomer, a prepolymer, namely a dimer, trimer or oligomer, a mixture thereof or a copolymer thereof. Examples of monomers and copolymers thereof include unsaturated carboxylic acids (such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid or maleic acid), esters thereof and amides thereof, and esters of unsaturated carboxylic acids and aliphatic polyvalent alcohols, and amides of unsaturated carboxylic acids and aliphatic polyvalent amine compounds, are used preferably. In addition, addition reaction products of unsaturated carboxylic acid esters or amides having a nucleophilic substituent such as a hydroxyl group, amino group or mercapto group and monofunctional or polyfunctional isocyanates or epoxy compounds, as well as dehydration condensation reaction products between monofunctional or polyfunctional carboxylic acids, are also used preferably. In addition, addition reaction products of unsaturated carboxylic acid esters or amides having an electrophilic substituent such as an isocyanate group or epoxy group and monofunctional or polyfunctional alcohols, amines or thiols, as well as substitution reaction products between unsaturated carboxylic acid esters or amides having a leaving substituent such as a halogen group or tosyloxy group and a monofunctional or polyfunctional alcohol, amines or thiol, are also preferable. In addition, other examples of compounds that can be used include groups of compounds in which an unsaturated phosphonic acid, styrene or vinyl ether and the like have been substituted instead of the above-mentioned unsaturated carboxylic acid.

[0070] Details regarding the manner in which these polymerizable compounds are used, such as their structure, independent or combined use or amount added, can be set arbitrarily according to the ultimate performance design of the lithographic printing plate precursor. These details are set based on, for example, the viewpoints indicated below.

[0071] With respect to sensitivity, a structure having a large number of unsaturated groups per molecule is preferable, and in many cases, a bifunctional or greater compound is preferable. In addition, in order to increase the strength of image areas, or in other words, the cured film, a trifunctional or greater compound is preferable, and a method that adjusts both sensitivity and strength by combining with the use of that having a different number of functional groups and different polymerizable groups (such as an acrylic ester, methacrylic ester, styrene-based compound or vinyl ether-based compound) is also effective.

[0072] In addition, selection and the manner of use of the polymerizable compound is also an important factor with respect to compatibility and dispersibility with other components in the image recording layer (such as a binder polymer, polymerization initiator, colorant and the like), and for example, compatibility can be improved by using compounds having low purity or combining the use of two or more types. In addition, a specific structure can also be selected for the purpose of improving adhesion with the support or oxygen-blocking protective layer and the like.

[0073] The above-mentioned polymerizable compound is preferably used within the range of 5% by weight to 80% by weight and more preferably 25% by weight to 75% by weight in the image recording layer. In addition, these may be used alone or two or more types may be used in combination. In addition, the manner in which the polymerizable compound is used is such that a suitable structure, incorporation and amount added can be arbitrarily selected from the viewpoints of the degree of inhibition of polymerization with respect to oxygen, resolution, fogging, changes in refractive index, surface adhesiveness and the like, and depending on the case, a layered configuration and coating method such as undercoating or topcoating can also be carried out.

[Other Components of Image Recording Layer]

[0074] Components other than the above-mentioned components (A), (B) and (C), such as binder polymers, surfactants, printout agents, polymerization inhibitors (thermal polymerization inhibitors), higher fatty acid derivatives, plasticizers, inorganic fine particles or low molecular weight hydrophilic compounds can be contained in the image recording layer.

[0075] A conventionally known binder polymer can be used without limitation for the binder polymer, and linear organic polymers capable of forming a film are preferable. Examples of such binder polymers include acrylic resins, polyvinyl acetal resins, polyurethane resins, polyurea resins, polyimide resins, polyamide resins, epoxy resins, methacrylic resins, polystyrene resins, novolac-type phenolic resins, polyester resins, synthetic rubbers, and natural rubbers.

[0076] A single binder polymer may be used alone or two or more types may be used as a mixture. The content of the binder polymer is preferably 10% by weight to 90% by weight and more preferably 20% by weight to 80% by weight

based on the total solid fraction of the image recording layer. If within these ranges, favorable strength of the image areas and favorable image formability are obtained. In addition, the polymerizable compound and the binder polymer are preferably used at a weight ratio of 1/9 to 7/3.

[0077] A surfactant can be used in the image recording layer to promote on-press developability at the start of printing and to improve coated surface properties. Examples of surfactants include nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, fluorine-based surfactants and the like. The surfactant may be used alone or two or more types may be used in combination.

[0078] The surfactant can be used alone or two or more types can be used in combination. The surfactant is preferably contained in the image recording layer at 0.001% by weight to 10% by weight and more preferably contained at 0.01% by weight to 5% by weight.

[0079] A dye that absorbs strongly in the visible light region can be used as a colorant in the image recording layer. Specific examples include Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS, and Oil Black T-505 (the preceding are products of Orient Chemical Industries, Ltd.), as well as Victoria Pure Blue, Crystal Violet (CI 42555), Methyl Violet (CI 42535), Ethyl Violet, Rhodamine B (CI 145170B), Malachite Green (CI 42000), Methylene Blue (CI 52015), and the dyes described in Japanese Patent Application Publication No. S62-293247. In addition, pigments such as phthalocyanine pigments, azo pigments, carbon black, titanium oxide and the like can also be used preferably.

[0080] The addition of these colorants is preferable since their use facilitates discrimination of the image areas from the nonimage areas following image formation. Furthermore, the colorant is preferably added at a ratio of 0.01% by weight to 10% by weight in the image recording layer.

[0081] A compound that changes color due to the action of acid or radicals can be added to the image recording layer of the present invention in order to produce a printout image. Various types of dyes are effectively used for this compound, examples of which include diphenylmethane types, triphenylmethane types, thiazine types, oxazine types, xanthene types, anthraquinone types, iminoquinone types, azo types, azomethine types and the like.

[0082] A small amount of polymerization inhibitor is preferably added to prevent unwanted thermal polymerization of the polymerizable compound (C) during production or storage of the image recording layer.

[0083] Suitable examples of the thermal polymerization inhibitor include hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butylcatechol, benzoquinone, 4,4'-thiobis (3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), and N-nitroso-N-phenylhydroxylamine aluminum salt.

[0084] The thermal polymerization inhibitor is preferably contained at about 0.01% by weight to about 5% by weight in the image recording layer.

[0085] A higher fatty acid derivative and the like in the manner of behenic acid or behenamide may be added to the image recording layer to prevent inhibition of polymerization by oxygen, and may be partitioned on the surface of the image recording layer during the course of drying after coating. The amount of the higher fatty acid derivative added is preferably about 0.1% by weight to about 10% by weight based on the total solid fraction of the image recording layer.

[0086] The image recording layer is formed by preparing a coating liquid by dispersing or dissolving the above-mentioned constituents in a suitable solvent and then coating the coating liquid.

[0087] The image recording layer can also be formed by preparing a plurality of coating liquids in which each of the same or different components are dispersed or dissolved in the same or different solvent followed by repeatedly coating and drying a plurality of times. The coated amount (solid fraction) on the image recording layer is preferably 0.3 g/m² to 1.5 g/m² and more preferably 0.5 g/m² to 1.5 g/m².

[0088] Various methods can be used for the coating method. Examples of coating methods include bar coating, spin coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, roll coating and the like.

[0089] There are no particular limitations on the support used in the lithographic printing plate precursor provided it is in the shape of a dimensionally stable plate. Examples of materials of the support include paper, plastic-laminated paper (such as polyethylene, polypropylene, polystyrene and the like), metal plate or sheet (such as aluminum, zinc, copper and the like), plastic film (such as cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetal and the like), and paper or plastic film on which any of the above-mentioned metals has been laminated or vapor-deposited. Preferable examples of the support include a polyester film and an aluminum sheet. An aluminum sheet is particularly preferable due to its dimensional stability and comparatively low cost.

[0090] The lithographic printing plate precursor may also be further provided with a backcoating or undercoating.

[Platemaking and Printing]

[0091] The lithographic printing plate precursor as previously described is imagewise exposed by exposing through an original image having a line image or halftone image or by scanning and exposing with a laser according to digital data. Examples of the exposure light source include a carbon arc lamp, high-pressure mercury lamp, xenon lamp, metal

halide lamp, fluorescent lamp, tungsten lamp, halogen lamp, ultraviolet laser, visible light laser and infrared laser. A laser is particularly preferable, and examples thereof include solid-state lasers and semiconductor lasers that emit infrared light at a wavelength of 760 nm to 1200 nm and semiconductor lasers that emit light at a wavelength of 250 nm to 420 nm. In the case of using a laser, imagewise scanning and exposure are preferably carried out in accordance with digital data. In addition, a multibeam laser device is preferably used to shorten exposure time.

[0092] There are no particular limitations on the method of using the fountain solution for the lithographic printing plate. After exposing the lithographic printing plate precursor in the manner described above, the unwanted image recording layer can be dissolved and removed with a suitable developing solution followed by supplying an oil-based ink and the fountain solution to the plate surface and printing.

[0093] Alternatively, after having imagewise exposed the lithographic printing plate precursor as described above with laser light, an oil-based ink and the fountain solution can be supplied without having to go through any type of development processing step followed by printing. Namely, a method referred to as on-press development can be employed in which a lithographic printing plate is obtained by removing nonimage areas while on the printing press during the course of printing.

[0094] Specific examples of this method include a method in which the lithographic printing plate precursor is exposed with laser light followed by mounting on the printing press and printing without going through a development processing step, and a method in which the lithographic printing plate precursor is mounted on the printing press followed by exposing with laser light while on the printing press and then printing without going through a development processing step.

[0095] When printing is carried out by imagewise exposure of the lithographic printing plate precursor with laser light followed by supplying the fountain solution and oil-based ink without going through a development processing step such as a wet development processing step, the image recording layer that has been cured by exposure forms an oil-based ink receptive area having an oleophilic surface in exposed areas of the image recording layer. On the other hand, in the unexposed areas, the uncured image recording layer is removed by being dissolved or dispersed by the supplied fountain solution and/or oil-based ink, and a hydrophilic surface is exposed in those areas. As a result, printing begins with the fountain solution component adhered to the exposed hydrophilic surface and the oil-based ink is taken up by the exposed areas of the image recording layer. Here, although the fountain solution or the oil-based ink may be supplied to the plate surface first, the oil-based ink is preferably supplied first from the viewpoint of preventing the fountain solution from being contaminated by the unexposed areas of the image recording layer.

[0096] In this manner, the lithographic printing plate precursor is developed on-press on an offset printing press and is used as is for printing a large number of sheets.

[0097] The emulsified plate cleaning agent for a lithographic printing plate of the present invention can be used to remove scumming based on causes occurring during platemaking, during subsequent storage or printing, or in all other stages from platemaking to printing.

[0098] The emulsified plate cleaning agent for a lithographic printing plate of the present invention is used by containing in a cloth or sponge and the like, wiping off any greasy locations or the entire side of the plate, and allowing to stand for about 30 seconds and finally wiping with water.

EXAMPLES

[0099] Although the following provides an explanation of the present invention through examples thereof, the present invention is not limited to these examples. Furthermore, the terms "parts" and "percent (%)" refer to parts by weight and percent (%) by weight, respectively, unless specifically indicated otherwise.

[Preparation of Emulsified Plate Cleaning Agent]

Example 1

[0100] 5 parts by weight of water-soluble soybean polysaccharide were dissolved in 53 parts by weight of pure water while warming. Next, 2 parts by weight of sodium metaphosphate were dissolved while stirring followed by the addition of 0.5 parts by weight of sulfuric acid, 0.5 parts by weight of nitric acid and 3 parts by weight of potassium hydroxide and mixing to prepare an aqueous phase. Moreover, the pH of the aqueous phase was adjusted to 2.0 by adding phosphoric acid a little at a time. On the other hand, an oil phase as prepared by dissolving 15 parts by weight of Swasol 1000, 15 parts by weight of Exxsol D-40, 2 parts by weight of Pelex OT-P, 1 part by weight of Nonion OP-80 and 1 part by weight of Paionin D-212. Next, the aqueous phase prepared in the manner described above was stirred and warmed to adjust to 35°C, then the oil phase was slowly added dropwise thereto to prepare a dispersion, and then passing through a homogenizer to fabricate a milky white, emulsified plate cleaning agent.

[0101] The plate cleaning agent obtained in this manner had a pH of 2.0, the same as that of the aqueous phase.

Examples 2 to 7 and Comparative Examples 1 to 12

[0102] Emulsified plate cleaning agents were fabricated according to the same procedure as that of the above-mentioned Example 1 with the exception of changing the composition.

[0103] The compositions of the emulsified plate cleaning agents of Examples 1 to 7 and Comparative Examples 1 to 12 are shown in the following Tables 1 to 3 (units of components: parts by weight). Furthermore, pH values of each of the emulsified plate cleaning agents, total amount of cations originating in contained salts (wt%), and the ratio of at least one type of cation selected from the group consisting of potassium, cesium and rubidium based on the total amount of cations (wt%) are also shown in the tables.

[Fabrication of Lithographic Printing Plate Precursors]

(1) Fabrication of Support

[0104] Degreasing treatment was carried out for 30 seconds at 50°C using a 10% by weight aqueous sodium aluminate solution in order to remove the rolling oil on the surface of a 0.3 mm thick aluminum sheet (material: JIS A 1050). Following degreasing, the aluminum surface was then grained using three nylon brushes implanted with bristles having a diameter of 0.3 mm and using an aqueous suspension (specific gravity: 1.1 g/cm³) of pumice having a median diameter of 25 μm followed by rinsing well with water. This sheet was then etched by immersion for 9 seconds in a 25% by weight aqueous sodium hydroxide solution at 45°C then rinsed with water, followed by immersing for 20 seconds in 20% by weight nitric acid at 60°C and rinsing with water. The amount of etching of the grained surface at this time was approximately 3 g/m².

[0105] Next, continuous electrochemical surface roughening treatment was subsequently carried out using 60 Hz alternating current voltage. The electrolyte solution was a 1% by weight aqueous nitric acid solution (containing 0.5% by weight of aluminum ions) and the liquid temperature was 50°C. The electrochemical surface roughening treatment was carried out with an alternating current power source waveform using trapezoidal square wave alternating current with a time required for the current value to go from zero to peak (TP) of 0.8 msec and a duty ratio of 1:1 and using a carbon electrode for the counter electrode. Ferrite was used for the auxiliary anode. The current density was 30 A/dm² at the peak current value, and 5% of the current flowing from the power source was branched to the auxiliary anode. The amount of electricity during nitric acid electrolysis was 175 C/dm² for the time during which the aluminum sheet served as an anode. This was followed by rinsing by spraying with water.

[0106] Continuing, electrochemical surface roughening treatment was carried out by the same method as for the nitric acid electrolysis using a 0.5% by weight aqueous hydrochloric acid solution (contained 0.5% by weight of aluminum ions) for the electrolyte and using an electrolyte temperature of 50°C and a quantity of electricity for the time during which the aluminum sheet served as an anode of 50 C/dm². This was followed by rinsing by spraying with water.

[0107] Next, a 2.5 g/m² direct current anodic oxidation coating was provided on this sheet using 15% by weight sulfuric acid (containing 0.5% by weight of aluminum ions) for the electrolyte and using a current density of 15 A/dm², followed by rinsing with water and drying to fabricate a support (1).

[0108] Subsequently, in order to ensure hydrophilicity of the nonimage regions, silicate treatment was carried out to the support (1) for 10 seconds at 60°C using a 2.5% by weight aqueous #3 sodium silicate solution followed by rinsing with water to obtain a support (2). The amount of Si adhered to the support was 10 mg/m². The center-line average roughness (Ra) of this substrate was 0.51 μm as measured using a needle having a diameter of 2 μm.

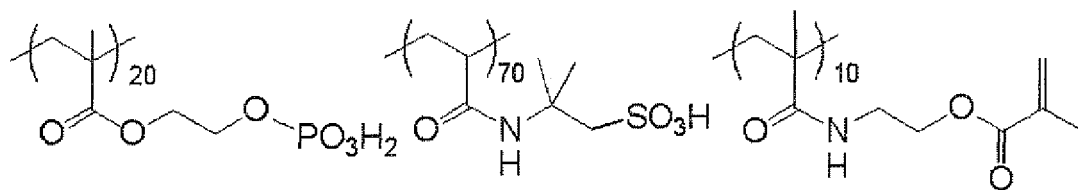
(2) Formation of Undercoat Layer

[0109] Next, an undercoat layer coating liquid (1) described below was coated onto the above-mentioned support (2) to a dry coating weight of 20 mg/m² to fabricate a support having an undercoat layer used in the following experiments.

<Undercoat Layer Coating Liquid (1)>

[0110]

* Undercoat layer compound (1) having structure indicated below	0.18 g
* Hydroxyethylimino diacetic acid	0.10 g
* Methanol	55.24 g
* Water	6.15 g



Undercoat Layer compound (1)

(Mw100,000)

(3) Formation of Image Recording Layer

[0111] An image recording layer coating liquid (1) having the following composition was bar-coated onto the undercoat layer formed in the manner described above followed by oven-drying for 60 seconds at 100°C to form an image recording layer having a dry coating weight of 1.0 g/m².

[0112] The image recording layer coating liquid (1) was obtained by mixing and stirring the following photosensitive liquid (1) with a microgel liquid (1) immediately before coating.

<Photosensitive Liquid (1)>

[0113]

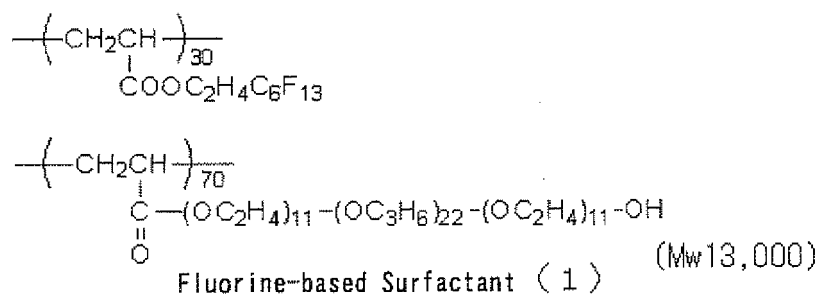
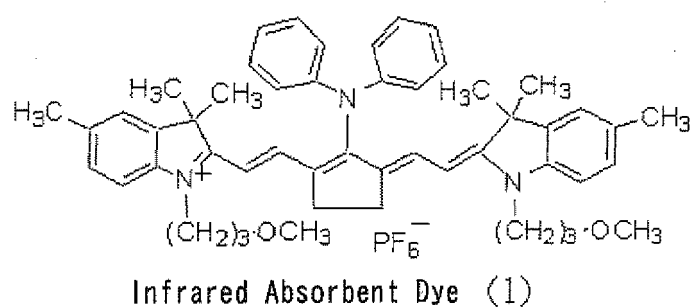
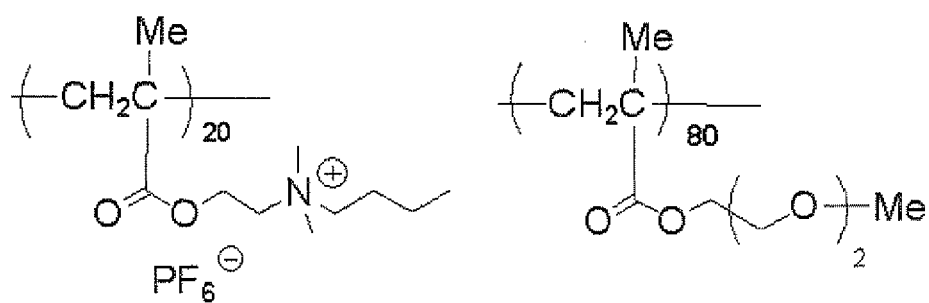
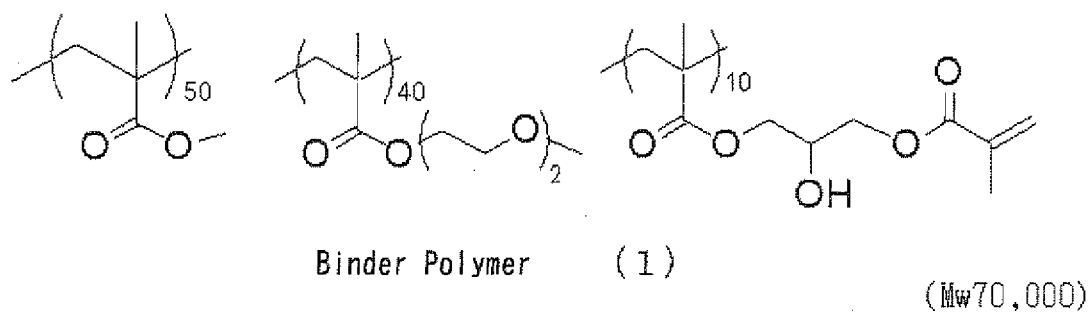
* Binder polymer (1) (structure below)	0.240 g
* Infrared absorbent dye (1) (structure below)	0.030 g
* Radical generator (1) (structure below)	0.162 g
* Radical polymerizable compound:	
Tris(acryloyloxyethyl)isocyanurate	
(NK-Ester A-9300, Shin-Nakamura Chemical Co., Ltd.)	0.192 g
* Low molecular weight hydrophilic compound:	
Tris(2-hydroxyethyl)isocyanurate	0.062 g
* Low molecular weight hydrophilic compound (1)	
(structure below)	0.050 g
* Oleosensitizer: Phosphonium compound (1)	
(structure below)	0.055 g
* Oleosensitizer: Benzyltrimethyloctylammonium·PF ₆ salt	0.018 g
* Oleosensitizer: Ammonium group-containing polymer	
(structure below, reduced specific viscosity: 44 cSt/g/ml)	0.035 g
* Fluorine-based surfactant (1) (structure below)	0.008 g
* 2-butanone	1.091 g
* 1-methoxy-2-propanol	8.609 g

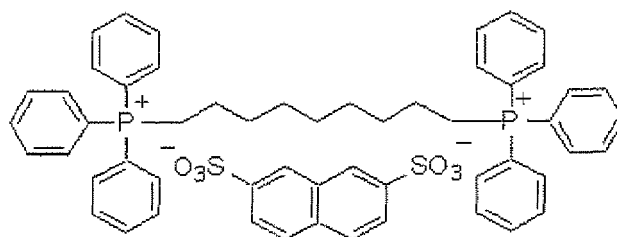
<Microgel Liquid (1)>

[0114]

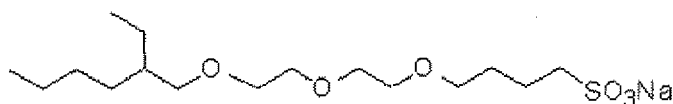
* Microgel (1)	2.640 g
* Distilled water	2.425 g

[0115] The structures of the above-mentioned binder polymer (1), infrared absorbent dye (1), radical generator (1), phosphonium compound (1), low molecular weight hydrophilic compound (1), ammonium group-containing polymer and fluorine-based surfactant (1) are as shown below.

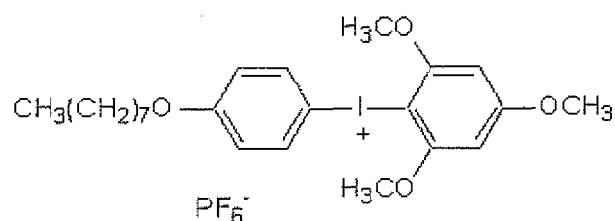




Phosphonium Compound (1)



Low Molecular Weight Hydrophilic Compound (1)



Radical Generator (1)

Synthesis of Microgel (1)

[0116] An oil phase component was prepared by dissolving 10 g of trimethylolpropane/xylene diisocyanate adduct (today's Mitsui Takeda Chemical Co., Ltd., Takenate D-110N), 3.15 g of pentaerythritol triacrylate (Nippon Kayaku Co., Ltd., SR444), and 0.1 g of Paionin A-41C (Takemoto Oil & Fat Co., Ltd.) in 17 g of ethyl acetate. 40 g of a 4% by weight aqueous solution of PVA-205 was prepared for the aqueous phase component. The oil phase component and aqueous phase component were mixed and emulsified for 10 minutes at 12,000 rpm using a homogenizer. The resulting emulsion was added to 25 g of distilled water and stirred for 30 minutes at room temperature and then for 3 hours at 50°C. The microgel liquid obtained in this manner was diluted with distilled water to a solid fraction concentration of 15% by weight of use as the above-mentioned microgel (1). Measurement of the average particle size of the microgel by a light scattering procedure yielded an average particle size of 0.2 μm.

(4) Formation of Protective Layer

[0117] A protective layer coating liquid (1) having the composition indicated below was further bar-coated onto the above-mentioned image recording layer followed oven-drying for 75 seconds at 125°C to form a protective layer having a dry coating weight of 0.15 g/m² and obtain a lithographic printing plate precursor.

[0118] Protective Layer Coating Liquid (1)

* Polyvinyl alcohol (PVA-405, Kuraray Co., Ltd., degree of saponification: 81.5 mol%, degree of polymerization: 500)	0.16 g
* Terminal sulfonic acid-modified polyvinyl alcohol (CKS-50, Nippon Synthetic Chemical Industry Co., Ltd.)	0.49 g
* Emalex 710 (Nihon Emulsion Co., Ltd., surfactant)	0.13 g

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(continued)

	* Inorganic layered compound dispersion (1)	22.28 g
	* Colloidal silica MP1040	
5	(Nissan Chemical Industries, Ltd., average particle size: 0.1 μm , 40% by weight aqueous solution)	0.30 g
	* Ion exchange water	52 g

(Preparation of Inorganic Layered Compound Dispersion (1))

10 **[0119]** 6.4 g of the synthetic mica Somashif ME-100 (Co-op Chemical Co., Ltd.) were added to 193.6 g of ion exchange water followed by dispersing to an average particle size of 3 μm (laser scattering method) using a homogenizer. The aspect ratio of the resulting dispersed particles was 100 or more.

15 **[0120]** Thus, a photopolymerizable lithographic printing plate precursor was obtained in which an oxygen-blocking protective layer containing an inorganic layered compound was provided on an image recording layer.

[Testing Methods]

20 **[0121]** Platemaking was carried out by on-plate development under the following printing conditions 1 or 2 using the photopolymerizable lithographic printing plate precursor obtained in the manner described above, followed by testing the performance of various types of plate cleaning agents.

<Printing Conditions 1>

25 **[0122]** Printing press: Heidelberg MOV (ALCOLOR, fountain solution supply device)

Ink: Environmentally-friendly Non-VOC ink (Toyo Ink Co., Ltd.,
TK NEX NV100 processed red ink)

Fountain solution: PressMax 30.33 fountain solution
(Fuji Hunt Photographic Chemicals Inc.) diluted to 4%

30 Platemaking conditions: After forming an image of the FM Screen TA FFTA 20 using the Quantum Thermal Laser Setter manufactured by Creo Co., Ltd., the plate was mounted on the printing press followed by supplying fountain solution and ink, completing on-press development and carrying out the printing tests described below.

<Scum Removal>

35 **[0123]** The following treatments (1, 2 and 3) were respectively carried out on nonimage areas of the plate on which on-press development had been completed.

40 **[0124]** When printing was resumed, adhesion of ink and scumming occurred on the treated areas. The various plate cleaning agents were soaked into a sponge, the entire side of the plate was wiped five times to remove scum after which printing was resumed. The ability of the plate to recover from scumming was then evaluated.

1. Air oxidation scumming: The plate was left for 3 hours in the printing press at 150°C without coating with gum.
2. Scratching: Scratches were made while applying a load of 100 g, 200 g or 300 g to a diamond stylus 4R using a scratch tester (Shinto Scientific Co., Ltd.) followed by allowing to stand in air for 3 days.
- 45 3. Oil scumming: 1 g of oleic acid was dissolved in 10 g of mineral spirits followed by soaking into absorbent cotton and buff drying.

[0125] Recovery from each of the types of scumming 1 to 3 described above was evaluated according to the criteria indicated below.

- 50 1. Removal of air oxidation scumming: Evaluation of removal of scumming for 100 impressions.

[0126] O: Superior

Δ : Somewhat inferior

55 $\times$: Inferior

2. Scratching: Evaluation of scratching for 100 impressions

[0127] O: Superior

Δ: Somewhat inferior

×: Inferior

3. Oil scumming: Evaluation of removal of soiling for 100 impressions

[0128] O: Superior

Δ: Somewhat inferior

×: Inferior

<Printing Conditions 2>

[0129] Printing press: New DAIYA (Mitsubishi Heavy Industries, Ltd.)

Ink: Printing ink (DIC Graphics Corp., sheet-fed ink,

Fusion G processed red ink)

Fountain solution: PressMax 30.33 fountain solution

(Fuji Hunt Photographic Chemicals Inc.) diluted to 4%

[0130] Platemaking conditions: After forming an image of the FM Screen TA FFTA 20 using the Quantum Thermal Laser Setter manufactured by Creo Co., Ltd., the plate was mounted on the printing press followed by supplying fountain solution and ink, completing on-plate development and carrying out the printing tests described below.

<Ink Adhesion>

[0131] The printing press was stopped after printing 1000 impressions on the plate on which on-plate development had been completed. The various plate cleaning agents were soaked into a sponge, the entire side of the plate was wiped five times after which printing was resumed. Adhesion of ink on solid image areas and halftone image areas during the time from the start of printing to printing of 2000 impressions was evaluated according to the following criteria from the viewpoints of the occurrence of uneven wiping and ink adhesion.

4. Occurrence of uneven wiping: Evaluated as number of impressions from start of printing to time when uneven wiping no longer occurred

[0132] O: No uneven wiping at start or 50 impressions or less printed until no longer observed

OA: 50 to 100 impressions until no longer observed Δ: 100 to 500 impressions until no longer observed

Δ×: 500 or more impressions until no longer observed

×: Uneven wiping still observed even after printing 2000 impressions

5. Ink adhesion: Evaluation of number of impressions from start of printing

[0133] until ink completely adhered

O: Ink completely adhered in 50 impressions or less

OA: Ink completely adhered in 50 to 100 impressions

Δ: Ink completely adhered in 100 to 500 impressions

Δ×: Ink completely adhered in 500 or more impressions

×: Ink not completely adhered even after 2000 impressions

[0134] The test results are described in the following tables.

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[Table 1]

		Examples						
		1	2	3	4	5	6	7
Aqueous Phase	Pure Water	53	53	53	53	53	53	55
	Water-soluble soybean polysaccharide	5	5	5	5	5	5	5
	Sodium metaphosphate	2	2	2	2	2	2	2
	Sulfuric acid	0.5	0.5	0.5	0.5	0.5	0.5	0.15
	Nitric acid	0.5	0.5	0.5	0.5	0.5	0.5	0.15
	Aqueous ammonia	-	-	-	-	-	-	-
	LiOH	-	-	-	-	-	-	-
	NaOH	-	-	-	1	1.5	2	0.35
	KOH	3	-	-	2	1.5	1	1
	RbOH	-	3	-	-	-	-	-
	CsOH	-	-	3	-	-	-	-
	Be(OH) ₂	-	-	-	-	-	-	-
	Mg(OH) ₂	-	-	-	-	-	-	-
	Ca(OH) ₂	-	-	-	-	-	-	-
	Ba(OH) ₂	-	-	-	-	-	-	-
	Phosphoric acid	Added a little at a time to adjust to pH 2.0						
Oil Phase	Swasol 1000	15	-	-	7.5	-	15	15
	Swasol 1500	-	15	-	7.5	15	-	-
	Swasol 200	-	-	15	-	-	-	-
	Exxsol D-40	15	-	-	7.5	-	-	-
	Exxsol D-80	-	15	-	7.5	-	-	-
	Exxsol D-110	-	-	15	-	15	15	15
	Pelex OT-P	2	2	2	2	2	2	2
	Nonion OP-80	1	1	1	1	1	1	1
	Paionin OP-212	1	1	1	1	1	1	1
Total		100	100	100	100	100	100	100
pH Value		2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total cation content (wt%)		2.61	3.03	3.18	2.49	2.43	2.38	0.77
K,Cs,Rb content/total cation content (wt%)		80.0	82.7	83.6	55.9	43.0	32.2	31.8
Test Results	Air oxidation scumming	○	○	○	○	○	○	○
	Scratch recovery	○	○	○	○	○	○	Δ
	Oil scumming	○	○	○	○	○	○	○
	Uneven wiping	○	○	○	○	○	○	○
	Ink adhesion	○	○	○	○	○	○	○

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[Table 2]

		Comparative Examples						
		1	2	3	4	5	6	7
Aqueous phase	Pure Water	50	53	53	53	53	53	53
	Water-soluble soybean polysaccharide	5	5	5	5	5	5	5
	Sodium metaphosphate	2	2	2	2	2	2	2
	Sulfuric acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Nitric acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Aqueous ammonia	6	-	-	-	-	-	-
	LiOH	-	3	-	-	-	-	-
	NaOH	-	-	3	-	-	-	-
	KOH	-	-	-	-	-	-	-
	RbOH	-	-	-	-	-	-	-
	CsOH	-	-	-	-	-	-	-
	Be(OH) ₂	-	-	-	3	-	-	-
	Mg(OH) ₂	-	-	-	-	3	-	-
	Ca(OH) ₂	-	-	-	-	-	3	-
	Ba(OH) ₂	-	-	-	-	-	-	3
	Phosphoric acid	Added a little at a time to adjust to pH 2.0						
Oil Phase	Swasol 1000	15	-	-	15	-	-	15
	Swasol 1500	-	15	-	-	15	-	-
	Swasol 200	-	-	15	-	-	15	-
	Exxsol D-40	15	-	-	15	-	-	15
	Exxsol D-80	-	15	-	-	15	-	-
	Exxsol D-110	-	-	15	-	-	15	-
	Pelex OT-P	2	2	2	2	2	2	2
	Nonion OP-80	1	1	1	1	1	1	1
	Paionin OP-212	1	1	1	1	1	1	1
Total		100	100	100	100	100	100	100
pH Value		2.0	2.0	2.0	2.0	2.0	2.0	2.0
Total cation content (wt%)		2.08	1.39	2.25	1.15	1.77	2.15	2.63
K,Cs,Rb content/total cation content (wt%)		0	0	0	0	0	0	0
Test Results	Air oxidation scumming	○	○	○	Δ	Δ	Δ	Δ
	Scratch recovery	○	○	○	○	○	○	Δ
	Oil scumming	○	○	○	Δ	Δ	Δ	Δ
	Uneven wiping	Δ×	×	×	×	Δ×	Δ×	Δ×
	Ink adhesion	Δ	×	×	Δ	Δ×	Δ×	Δ×

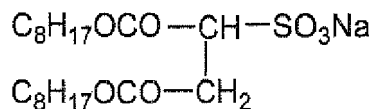
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[Table 3]

		Comparative Examples				
		8	9	10	11	12
Aqueous phase	Pure Water	55	57	53	53	53
	Water-soluble soybean polysaccharide	5	5	5	5	5
	Sodium metaphosphate	-	2	2	2	2
	Sulfuric acid	0.04	-	0.5	0.2	0.08
	Nitric acid	0.04	-	0.5	0.2	0.08
	Aqueous ammonia	-	-	-	-	-
	LiOH	-	-	-	-	-
	NaOH	-	-	2.5	-	-
	KOH	0.1	-	0.5	0.5	0.2
	RbOH	-	-	-	-	-
	CsOH	-	-	-	-	-
	Be(OH) ₂	-	-	-	-	-
	Mg(OH) ₂	-	-	-	-	-
	Ca(OH) ₂	-	-	-	-	-
	Ba(OH) ₂	-	-	-	-	-
	Phosphoric acid	Added a little at a time to adjust to pH 2.0				
Oil Phase	Swasol 1000	15	-	-	7.5	7.5
	Swasol 1500	-	-	15	7.5	7.5
	Swasol 200	-	15	-	-	-
	Exxol D-40	-	-	-	7.5	7.5
	Exxsol D-80	-	-	15	7.5	7.5
	Exxsol D-110	15	15	-	-	-
	Pelex OT-P	2	2	2	2	2
	Nonion OP-80	1	1	1	1	1
	Paionin OP-212	1	1	1	1	1
Total		100	100	100	100	100
pH Value		2.0	2.0	2.0	2.0	2.0
Total cation content (wt%)		0.14	0.52	2.31	0.87	0.66
K,Cs,Rb content/total cation content (wt%)		49.0	0	15.9	15.1	21.0
Test Results	Air oxidation scumming	Δ	×	○	Δ	Δ
	Scratch recovery	×	×	Δ	Δ	Δ
	Oil scumming	×	×	○	Δ	Δ
	Uneven wiping	○	Δ	Δ	○Δ	○Δ
	Ink adhesion	○	Δ×	Δ	○Δ	○Δ

[0135] Furthermore, the components contained in the oil phase were as indicated below.
 Swasol 1000 (aromatic, high boiling point solvent, Maruzen Petrochemical Co., Ltd.)
 Swasol 1500 (aromatic, high boiling point solvent, Maruzen Petrochemical Co., Ltd.)

Swasol 2000 (aromatic, high boiling point solvent, Maruzen Petrochemical Co., Ltd.)
 Exxol D-40 (naphthene-based solvent, Exxon Mobil Corporation)
 Exxsol D-80 (naphthene-based solvent, Exxon Mobil Corporation)
 Exxsol D-110 (naphthene-based solvent, Exxon Mobil Corporation)
 Pelex OT-P (sodium dialkylsulfosuccinate, Kao Corp.)
 Active ingredient: 70%



Nonion OP-80 (sorbitan monooleic acid, NOF Corp.)
 Paionin D-212 (polyoxyethylene castor oil ether, Takemoto Oil & Fat Co., Ltd.)

Claims

1. An emulsified plate cleaning agent for a lithographic printing plate, which is used on a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, wherein the total cation content of a contained salt based on the total weight of the plate cleaning agent is 0.5% by weight or more, and 30% by weight or more of the cations are at least one type selected from the group consisting of potassium, cesium and rubidium based on the weight of all cations.
2. The emulsified plate cleaning agent for a lithographic printing plate according to claim 1, which is used in a lithographic printing plate obtained by platemaking from a photopolymerizable lithographic printing plate precursor in which the oxygen-blocking protective layer contains inorganic fine particles.
3. A plate surface treatment method for a lithographic printing plate, the method comprising: cleaning a lithographic printing plate, obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer, with the emulsified plate cleaning agent for a lithographic printing plate according to claim 1 or claim 2.
4. The plate surface treatment method for a lithographic printing plate according to claim 3, wherein a lithographic printing plate, obtained by platemaking from a photopolymerizable lithographic printing plate precursor provided with an oxygen-blocking protective layer containing inorganic fine particles, is cleaned.



EUROPEAN SEARCH REPORT

Application Number
EP 12 15 5725

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 2003 054150 A (FUJI PHOTO FILM CO LTD) 26 February 2003 (2003-02-26) * paragraph [0060]; claims; example 4 * -----	1-3	INV. C11D17/00 C11D3/04 C11D11/00
X	JP 2001 277480 A (FUJI PHOTO FILM CO LTD) 9 October 2001 (2001-10-09) * paragraphs [0033], [0035]; claims; examples 2, 4 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 11 June 2012	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 12 15 5725

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The members are as contained in the European Patent Office EDP file on
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11-06-2012

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2003054150	A	26-02-2003	NONE	

JP 2001277480	A	09-10-2001	NONE	

REFERENCES CITED IN THE DESCRIPTION

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