(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 144 201**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **84308150.6**

(22) Date of filing: **23.11.84**

(51) Int. Cl.⁴: **B 41 N 3/08**

(30) Priority: **25.11.83 JP 220587/83**

(43) Date of publication of application:
12.06.85 Bulletin 85/24

(84) Designated Contracting States:
DE GB

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(54) Plate cleaner for electrophotolithographic printing plate.

(57) A plate cleaner for an electrophotolithographic printing plate and a process for preventing background stains of a lithographic plate using the plate cleaner are described, comprising a suspension or an emulsion containing as main component (1) a water solution of a compound capable of producing a hydrophilic substance by reaction with zinc oxide, (2) a hydrocarbon solvent, and (3) a surface active agent to remove background contamination from a plate surface.

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PLATE CLEANER FOR ELECTROPHOTO-LITHOGRAPHIC PRINTING PLATE

FIELD OF THE INVENTION

The present invention relates to a plate cleaner for a lithographic printing plate which is made by an electrophotographic process.

BACKGROUND OF THE INVENTION

If an electrophotographic process is employed for making a lithographic printing plate, the printing plate can be easily made through only simple procedures of forming an image according to ordinary electrophotographic steps, and then wiping the copied surface of an electrophotographic photoreceptor with such a desensitizing solution (also called etching solution) as to render the non-image area hydrophilic, that is to say, only procedures requiring no special techniques.

For instance, photoconductive zinc oxide is coated together with a binder on a base paper which has previously been so treated as to have a water resisting property. The thus-formed photoconductive layer is subjected to corona discharge or the like to gain charges electrostatically. Then, it is exposed to a light pattern in the dark, whereby charges in the exposed areas are dissipated and those in the non-exposed areas remain. Thus, electrostatic latent image is created on

the photoconductive layer. The latent image is developed by then spraying charged toner particles onto the photoconductive layer or dipping the photoconductive layer in an insulating liquid in which charged particles are dispersed, thereby causing the charged toner particles to adhere thereto by Coulombic attraction in an imagewise pattern.

In general, toner particles used in a developer are coated with an oleophilic resin, and fixed to a photoconductive layer by a process of heat sealable adhesion or evaporation of solvent.

Thus, the image part displays an oleophilic property due to the oleophilic resin coat of toner particles. In order to convert an electrophotographic copy obtained thereby to a lithographic printing plate, it is necessary for the non-image part to be rendered hydrophilic. Such can be done, for example, in the following manner. When the copied face is wetted with a desensitizing solution which can convert certain substances into those having a strong affinity for water, e.g., a solution in which potassium ferrocyanide, potassium ferricyanide, ammonium phosphate or so on is dissolved, it is observed that a film of a water-insoluble precipitate (e.g., $K_2Zn_3[Fe(CN)_6]_2$, $ZnNH_4PO_4$, etc.) is formed in the part to be rendered hydrophilic

by the reaction of the above-described solute with zinc oxide which constitutes the photoconductive layer. The operation is very simple, since it suffices for the wetting procedure to simply wipe the copied face with absorbent cotton or gauze dampened with a solution as above described.

Preferred desensitizing solutions are explained in detail in U.S. Patents 3,001,871, 3,592,640 and 4,208,212.

When printing from a lithographic printing plate obtained by the above-described procedure, the hydrophilic property of the non-image part tends to deteriorate for one reason or another. Ink often sticks to such areas, causing so-called background contamination. A typical cause of background contamination, though the contamination is attributed to a wide variety of causes, involves the drying of the plate surface after treatment for rendering hydrophilic. When the plate surface is dried, it happens that ink adheres to the dried areas in spots or over the whole plate surface at the time of printing. A phenomenon like this can be also observed when a printing machine is stopped in the course of printing on account of machine trouble or for the purpose of taking a rest. Another cause involves adhesion of oleophilic substances to an uncovered hydrophilic layer. In this

case, the adhesion spots become ink-receptive, and are turned into stains. Also, it can be attributed to a similar cause, viz., fingerprints, which have been left on the hydrophilic layer before treatment for rendering the non-image part of the photoconductive layer hydrophilic, make their appearance at the background of printed matter.

Hitherto, in the case of a typical PS plate (which is the abbreviation of Pre-Sensitized printing plate, that is to say, a lithographic printing plate to which photosensitivity is imparted in advance) the stains can be removed by wiping with dampening water or an etching solution and thereby the plate surface can be restored to the original state to some degree. On the other hand, an electrophoto-lithographic printing plate has a strong affinity for printing ink, and therefore the stains can hardly be changed for the better by wiping with an etching solution or a washing oil. In addition, although various kinds of plate cleaner have been provided for PS plates, application of such cleaner to electrophoto-lithographic printing plates cannot reduce the background contamination due to their insufficient effect upon removal of the printing ink, and, what is worse, it happens that the photoreceptive layer of an

electrophoto-lithographic printing plate is destroyed by application of such cleaner to rather generate stains. Such being the case, cleaners fit for practical use have not yet been presented, and the advent of a plate cleaner specifically for use with an electrophoto-lithographic printing plate's exclusive use has been ardently desired.

SUMMARY OF THE INVENTION

Therefore, a primary object of the present invention is to provide a plate cleaner for an electrophoto-lithographic printing plate which can restore the plate surface from stains generated in the course of printing operations, stains due to finger-prints or ink left on the plate surface before or after the treatment for rendering the non-image part of the photoconductive layer hydrophilic, or stains caused by scratches, and enables normal printing which is free from background contamination.

As a result of extensive investigations, it has now been found that the above-described object can be attained by using as a plate cleaner a suspension or an emulsion comprising as main components:

(1) an aqueous solution of a compound capable of producing a hydrophilic substance by reaction with zinc oxide,

(2) a hydrocarbon solvent having an action of dissolving lithographic printing ink, and

(3) a surface active agent.

In addition to the above-described principal components, the cleaner of the present invention may preferably additionally comprise the following components:

(4) a water-soluble collidal substance,

(5) a wetting agent, and

(6) at least one compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric acid, polyphosphoric acid, and water-soluble alkali metal salts thereof.

DETAILED DESCRIPTION OF THE INVENTION

Examples of compounds capable of producing hydrophilic substances by reacting with zinc oxide, which are employed as the component (1) in the present invention include ferrocyanide compounds such as potassium ferrocyanide, sodium ferrocyanide, etc.; ferricyanide compounds such as potassium ferricyanide, sodium ferricyanide, etc.; phosphoric acid compounds such as ammonium primary phosphate, ammonium secondary phosphate, etc.; phytic acid and the derivatives thereof, that is, phytic acid compounds, as described in Japanese Patent Application (OPI) No. 127002/78 (the term "OPI" as used herein refers to a "published unexamined Japanese patent application"); polyvalent metal salts such as ferric chloride, cupric chloride, etc.; hexamminecobalt salts,

hexamminenickel salts, EDTA (ethylenediaminetetraacetate) chelate compounds, and the like, as described in U.S. Patent 4,282,811; polyacrylic acid, sodium polyacrylate, polymethacrylic acid, sodium polymethacrylate, alginic acid, sodium alginate, cationic polymers such as melamine-formaldehyde resin, and so on. Compounds to be employed as the component (1) are not limited to any particular compounds, provided that they can react with zinc oxide to produce hydrophilic substances. Further, they can be used as a mixture of two or more thereof. It is preferred in the present invention to use these compounds in a condition of water solution. The water solution is preferably adjusted to a pH of from 2 to 6. It is advisable to use the above-described compounds in combination with an acid or a base such as ammonia, phosphoric acid, ammonium phosphate, citric acid, sodium citrate, or the like.

The hydrocarbon solvent of the component (2) employed in the present invention is one which has an action of dissolving lithographic printing ink, and an especially useful hydrocarbon solvent is a petroleum fraction ranging in boiling point from 120°C to 320°C, which is conventionally used in washing for removal of ink. This hydrocarbon solvent is generally used in an amount corresponding to from 5 to 50%, and preferably from 10 to 40%, of the total weight of the cleaner composition.

As the component (1) and the component (2) are immiscible, they are thoroughly mingled and dispersed and put to use in such a dispersed condition.

Preferred surface active agents forming the component (3) employed in the present invention are those having anionic or nonionic character, and have the function of enhancing dispersibility of the system. Examples of preferred anionic surface active agents include aliphatic salts, higher alcohol sulfate salts, aliphatic alcohol phosphate salts, sulfonic acid salts of dibasic fatty acid esters, fatty acid amide sulfonic acid salts, alkylarylsulfonic acid salts, and formaldehyde-condensed naphthalenesulfonic acid salts.

Examples of preferred nonionic surface active agents which can be used include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters, polyoxypropylene, polyoxyethylene ethers and so on. These surface active agents may be used in combinations of two or more thereof. The quantity of such surface active agents used in the cleaner is, though not particularly limited, preferably in the range of not more than 10% of the total weight of the cleaner composition.

Besides adding the surface active agent of the component (3), it is preferable in the present invention to add a water-soluble colloidal substance as a component

(4) for the purpose of further enhancing the dispersing stability of the cleaner.

Specific examples of preferred water-soluble colloidal substances which can be preferably used in the present invention include natural resins or modified resins thereof such as dextrin, gum arabic, shellac, alginic acid salts, cellulose deriva-tives (e.g., carboxymethyl cellulose, carboxyethyl cellulose, hydroxyethyl cellulose, methyl cellulose, etc.), and so on; and synthetic resins such as polyvinyl alcohol and the derivatives thereof, polyvinyl pyrrolidone, polyacrylamide and copolymers thereof, acrylic acid copolymers, vinyl methyl ether/maleic anhydride copolymers, vinyl acetate maleic anhydride copolymers, styrene/maleic anhydride copolymers, and so on. These substances can be used alone or as a mixture.

In addition to the above-described components, one or more wetting agents are also useful as a component (5) in the plate cleaner for the purpose of imparting an excellent spread characteristic and retarding the progress of drying and thereby making an improvement in using facility. Suitable wetting agents are compounds of the formula $HO\left(R\text{-}O\right)_{m}H$ [wherein R is C_nH_{2n} (n is an integer from 2 to 6) and m is from 1 to 500]. Of such compounds, ethylene glycol, propylene glycol, butylene

glycol, pentanediol, hexylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol, and the like are preferably used. Other wetting agents which can be used advantageously are glycerin, sorbitol, and pentaerythritol.

The characteristics of the plate cleaner of the present invention are that they can exert a very strong action preventing background contamination due to scratches the hydrophilic layer received, and perform a powerful function in maintaining or reinforcing the recovered hydrophilic property. Said characteristics are further intensified by using as the component (6) at least one compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric acid or polyphosphoric acid, and water-soluble alkali metal salts thereof together with the foregoing components. Such a compound as described above is typically used in a range of from 0.1 to 10%, and preferably from 0.2 to 5%, of the total weight of the cleaner composition.

The plate cleaner of the present invention may also contain in its composition granular powders such as pumice, alumina powder, silica powder and the like, colloidal silica, colloidal alumina, dyes and so on in addition to the above-described ingredients.

The present invention will now be illustrated in greater detail by reference to the following examples. However, the invention is not intended to be construed as being limited to these examples. Unless otherwise indicated, all parts and all percents are by weight.

EXAMPLE 1

In 70 parts of distilled water were dissolved 10 parts of glycerine, 10 parts of ammonium primary phosphate, 5 parts of potassium ferrocyanide, 2 parts of gum arabic and 3 parts of polyethylene glycol oleyl ether (Noigen ET-120, produced by Dai-ichi Kogyo Seiyaku Co., Ltd.), and the resulting solution was named Solution A.

Separately, 4 parts of sorbitol oleic acid monoester (Nissan Nonion OP-80, produced by Nippon Oils & Fats Co., Ltd.) was dissolved in 20 parts of n-heptane, and named Solution B.

Then, Solution B was slowly added dropwise to Solution A with stirring, and dispersed into Solution A. The resulting dispersion was made into a yellow emulsion by means of a homogenizer.

A lithographic printing plate was prepared by means of a commercially available offset master-making machine, ELP-280 (made by Fuji Photo Film Co., Ltd.). The electrophotographic light-sensitive material used in

the production of the printing plate was produced by coating the following composition on a waterproof paper rendered electroconductive to obtain a photoconductive layer having a dry thickness of 10 μ.

ZnO ("SAZEX 2000" produced by Sakai Kagaku Co., Ltd.)	80 g
Acrylic Resin ("Acrydic 54-127-60" produced by Dainihon Ink Co., Ltd.; 60% solution of an acrylic resin)	32 g
Methanol (solvent for the following sensitizer)	10 mℓ
Rose Bengale	0.13 g
Fluorescein	0.05 g
Bromophenol Blue	0.05 g
Toluene-Xylene (weight ratio: 1:1)	100 g

The developer used hereinabove had the following formulation.

Polyvinyl Acetate Particle (particle diameter: 0.2 μ)	3 g
Blend of Alkali Blue, a Poly(lauryl-methacrylate-acrylic acid) (monomer weight ratio = 10:1) and Isopar H (isoparaffinic solvent produced by Esso Petroleum Co., Ltd.) (weight ratio = 1:2:7)	1 g
Manganese Naphthenate	0.1 g
Isopar H	1,000 mℓ

After fingerprints were formed on a non-image area of the printing plate thus prepared, a desensitizing solution having the following composition was applied to the whole surface of the printing plate.

Desensitizing Solution:

$K_4Fe(CN)_6 \cdot 3H_2O$	3 g
$NH_4H_2PO_4$	6 g
Glycerin	10 g
Gum Arabic	0.5 g
Distilled Water	100 g

Then, the printing test was carried out using a printing machine Hamadastar 700 CD. As a result, generation of stains was observed on the part where fingerprints had been put. After 100 sheets of copies had been printed, the operation of the printing machine was suspended, and the finger marks (to which ink had already adhered) was wiped with the plate cleaner prepared herein and thereafter the printing machine was operated again. Thus, not less than 10,000 copies which had good quality and no finger marks were obtained. Of course, these copies showed no abnormality in the image part and others.

EXAMPLE 2

Both Solutions 2A and 2B having the following formulae respectively were prepared in the same manner as described in Example 1, and another plate cleaner was obtained.

Solution 2A

Water	54 parts
Polyvinyl Alcohol (PVAGH-17, trade name, produced by Nippon Synthetic Chemical Industry Co., Ltd.)	2 parts
Glycerin	10 parts
Phytic Acid (50% water solution, produced by Mitsui Toatsu Chemicals Inc.)	5 parts
Ammonia (25% water solution)	17 parts
Polyethylene Glycol Nonyl Phenyl Ether (Neigen EA-80, trade name, produced by Dai-ichi Kogyo Seiyaku Co., Ltd.)	2 parts

Solution 2B

Solvent K (trade name, product of Nippon Oil Company, Limited, petroleum fraction of b.p. of 140 to 205°C)	20 parts
Polyethylene Glycol Sorbitan Monostearate (Solgen TW, trade name, product of Dai-ichi Kogyo Seiyaku Co., Ltd.)	2 parts

A lithographic printing plate was made in the same manner as employed in Example 1 and finger marks were formed thereon with ink-stained fingers, followed by subjecting it to the same treatment for acquiring hydrophilic property with the desensitizing solution used in Example 1. Printing was carried out using the resulting printing plate, and stains of a fingerprint pattern were observed in the printed matter. After 100 copies had been printed, the operation of the printing machine was suspended, and the finger marks (to which

ink had already been sticked) were wiped with the above-described plate cleaner, and thereafter the printing machine was operated again. Thus, not less than 10,000 copies which had good quality and no finger marks were obtained. Furthermore, these copies showed no abnormality in the image part, e.g., no deterioration in inking.

EXAMPLE 3

Both solutions 3A and 3B having the following formulae respectively were prepared in the same manner as employed in Example 1, and still another plate cleaner was obtained.

Solution 3A

Water	55 parts
Triethylene Glycol	10 parts
Methyl Cellulose (Metholose 60SH-50, trade name, product of Shin-etsu Chemical Industry Co., Ltd.)	2 parts
Hexamminecobalt Chloride	2.5 parts
Ammonium Secondary Phosphate	5 parts
Silica Powder (Aerosil 380, trade name, product of Nippon Aerosil)	0.4 part
Sodium Borate	0.5 part
Polypropylene Glycol Ethylene Glycol Ether (Epan 420, trade name, product of Dai-ichi Kogyo Seiyaku Co., Ltd.)	2 parts

Solution 3B

Kerosene	20 parts
Sorbitan Monostearate (Solgen-50, trade name, product of Dai-ichi Kogyo Seiyaku Co., Ltd.)	2 parts
Benzyl Alcohol	1 part

A lithographic printing plate made in the same manner as employed in Example 1 was placed in a printing machine, Hamadastar 700 CD, and ink was put on a part of the plate surface using an inking roller. Then, the resulting plate was rendered hydrophilic using the etching solution used in Example 1. As a result of printing, intense printing stain was generated in the part where the inking had been carried out before the treatment for rendering hydrophilic. The operation of the printing machine was suspended, and the plate surface was wiped with the above-described cleaner. Thereafter, the operation was started again, and more than 10,000 copies which had good quality and no stain were obtained. Furthermore, these copies showed no abnormality in the image part.

EXAMPLE 4

A lithographic printing plate made in the same manner as employed in Example 1 was treated as to acquire an affinity for water, and printing was carried out using the resulting printing plate. Then, the printing operation was suspended, and the plate surface got scratches

by being rubbed with sandpaper. Thereafter, the printing machine was operated again. As a result, the scratching marks remained as stains on the prints. Therefore, the printing operation was suspended again, and the plate surface was wiped with the plate cleaner prepared in Example 1. Thereafter, more than 10,000 copies having good quality and no scratch stain were obtained. In addition, it was recognized similarly that the plate cleaner prepared in Example 2 and Example 3, respectively, had an improving effect (i.e., minimized) on scratch stain.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A plate cleaner for an electrophotolithographic printing plate which comprises a suspension or an emulsion containing as main components (1) a water solution of a compound which can produce a hydrophilic substance by reaction with zinc oxide, (2) a hydrocarbon solvent, and (3) a surface active agent.

2. A plate cleaner as in claim 1, wherein said compound of component (1) is selected from the group consisting of ferrocyanide compounds, ferricyanide compounds, phosphoric acid compounds, phytic acid compounds, polyvalent metal salts, hexamminecobalt salts, hexamminenickel salts, EDTA chelate compounds, poly-acrylic acid, sodium polyacrylate, polymethacrylic acid, sodium polymethacrylate, alginic acid, sodium alginate and cationic polymers.

3. A plate cleaner as in claim 1, wherein said surface active agent is an anionic or a nonionic surface active agent.

4. A plate cleaner as in claim 1, wherein said hydrocarbon solvent is petroleum fraction ranging in boiling point from 120°C to 320°C.

5. A plate cleaner as in claim 4, wherein said hydrocarbon solvent is contained therein in range of from 5 to 50 wt% of the total weight of the composition.

6. A plate cleaner as in claim 2, wherein said surface active agent is an anionic or nonionic surface active agent, and said hydrocarbon solvent is a petroleum fraction ranging in boiling point from 120°C to 320°C.

7. A plate cleaner as in claim 6, wherein said hydrocarbon solvent is contained therein in a range of from 5 to 50 wt% of the total weight of the composition.

8. A plate cleaner as in claim 1, wherein said cleaner additionally comprises as component (4) a water-soluble colloidal substance.

9. A plate cleaner as in claim 6, wherein said cleaner additionally comprises as component (4) a water-soluble colloidal substance.

10. A plate cleaner as in claim 1, additionally comprising a wetting agent component.

11. A plate cleaner as in claim 6, additionally comprising a wetting agent component.

12. A plate cleaner as in claim 1, additionally comprising a compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric acid, polyphosphoric acid, and water-soluble alkali metal salts thereof.

13. A plate cleaner as in claim 6, additionally comprising a compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric

acid, polyphosphoric acid, and water-soluble alkali metal salts thereof.

14. A plate cleaner as in claim 8, additionally comprising as component (5) a wetting agent.

15. A plate cleaner as in claim 9, additionally comprising as component (5) a wetting agent.

16. A plate cleaner as in claim 14, additionally comprising as component (6) a compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric acid, polyphosphoric acid, and water-soluble alkali metal salts thereof.

17. A plate cleaner as in claim 15, additionally comprising as component (6) a compound selected from the group consisting of molybdic acid, boric acid, nitric acid, phosphoric acid, polyphosphoric acid, and water-soluble alkali metal salts thereof.

18. A plate cleaner as in claim 14, wherein the water-soluble colloidal substance component (4) is at least one of a natural resin selected from the group consisting of dextrin, gum arabic, shellac, alginic acid salts, cellulose derivatives, and a synthetic resin selected from the group consisting of modified natural resins, polyvinyl alcohol and derivatives thereof, polyvinyl pyrrolidone, polyacrylamide and copolymers thereof, acrylic acid copolymers, vinyl methyl ether/

maleic anhydride copolymers, vinyl acetate/maleic anhydride copolymers, and styrene/maleic anhydride copolymers.

19. A plate cleaner as in claim 14, wherein said wetting agent component (5) is selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, pentanediol, hexylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, and tripropylene glycol.

20. A process for preventing background stains of a lithographic plate, comprising treating the lithographic plate surface which is produced by an electrophotographic process from an electrophotographic plate containing ZnO photoreceptor, with the plate cleaner defined in claim 1.