



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : G03F 7/07	A1	(11) International Publication Number: WO 93/11468 (43) International Publication Date: 10 June 1993 (10.06.93)
(21) International Application Number: PCT/EP92/02590 (22) International Filing Date: 11 November 1992 (11.11.92) (30) Priority data: 91203094.7 27 November 1991 (27.11.91) EP (34) Countries for which the regional or international application was filed: DE et al. (71) Applicant (for all designated States except US): AGFA-GEVAERT NAAMLOZE VENNOOTSCHAP [BE/BE]; Septestraat 27, B-2640 Mortsel (BE). (72) Inventors; and (75) Inventors/Applicants (for US only) : VAN DAMME, Marc [BE/BE]; COPPENS, Paul [BE/BE]; HOES, Eric [BE/BE]; Agfa-Gevaert N.V., DIE 3800, Septestraat 27, B-2640 Mortsel (BE).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: A METHOD FOR INCREASING THE HYDROPHOBICITY OF A SILVER IMAGE (57) Abstract The present invention provides a method for obtaining a lithographic printing plate comprising the steps of: information-wise exposing an imaging element comprising on a support a silver halide emulsion layer and a layer containing physical development nuclei, developing said information-wise exposed imaging element according to the DTR-process in the presence of developing agent(s) and silver halide solvent(s), treating the obtained silver image with a solution containing a hydrophobic polymer comprising mercapto groups. A thus obtained lithographic printing plate shows an increased printing endurance and the number of copies before a copy of constant quality is obtained is reduced.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

DESCRIPTION

A METHOD FOR INCREASING THE HYDROPHOBICITY OF A SILVER IMAGE.

1. Field of the invention.

The present invention relates to a method for hydrophobizing a silver image obtained according to the silver salt diffusion transfer process so that said silver image can be used in a lithographic printing process.

2. Background of the invention.

The principles of the silver complex diffusion transfer reversal process, hereinafter called DTR-process, have been described e.g. in US-P 2,352,014 and in the book "Photographic Silver Halide Diffusion Processes" by André Rott and Edith Weyde - The Focal Press - London and New York, (1972).

In the DTR-process non-developed silver halide of an information-wise exposed photographic silver halide emulsion layer material is transformed with a so-called silver halide solvent into soluble silver complex compounds which are allowed to diffuse into an image-receiving element and are reduced therein with a developing agent, generally in the presence of physical development nuclei, to form a silver image having reversed image density values ("DTR-image") with respect to the black silver image obtained in the exposed areas of the photographic material.

A DTR-image bearing material can be used as a planographic printing plate wherein the DTR-silver image areas form the water-repellant ink-receptive areas on a water-receptive ink-repellant background. The DTR-image can be formed in the image-receiving layer of a sheet or web material which is a separate element with respect to the photographic silver halide emulsion material (a so-called two-sheet DTR element) or in the image-receiving layer of a so-called single-support-element, also called mono-sheet element, which contains at least one photographic silver halide emulsion layer integral with an image-receiving layer

in water permeable relationship therewith. It is the latter mono-sheet version which is preferred for the preparation of offset printing plates by the DTR method.

To obtain a lithographic printing plate with good printing properties it is necessary to improve the hydrophobicity of the silver image obtained using the DTR-process. For this purpose hydrophobizing agents are used. These agents are commonly added to a processing liquid used during processing of an information-wise exposed DTR-imaging element e.g. to the developing liquid, the neutralization liquid etc.. Alternatively they may also be applied after development of the plate using a so-called finishing liquid or starter solution. Known hydrophobizing agents are e.g. those described in US-P 3,776,728, and US-P 4,563,410. Specific examples are 5-n-heptyl-2-mercapto-1,3,4,-oxadiazol and 3-mercapto-4-acetamido-5-n.heptyl-1,2,4-triazole.

Although the printing properties of a lithographic printing plate obtained according to the DTR-process can be improved using the above mentioned hydrophobizing agents some of these printing properties still need to be improved. For example the first copies obtained are generally of low quality and have to be disposed. For printing jobs requiring a small number of copies it is especially important to limit the number of initial copies that have to be disposed. On the other hand some printing jobs require a high printing endurance i.e. the quality of the copies needs to be constant over a large number of copies.

3. Summary of the invention.

It is an object of the present invention to provide a method for obtaining a lithographic printing plate according to the DTR-process using hydrophobizing agents by which the printing properties of said printing plate can be improved.

Further objects of the present invention will become clear from the description hereinafter.

According to the present invention a method is provided for obtaining a lithographic printing plate comprising the steps of developing an information-wise exposed imaging element according to

the DTR-process and treating said information-wise exposed imaging element during or after said development with a liquid containing a hydrophobic polymer comprising mercapto-groups.

4. Detailed description of the present invention.

It has been found that the printing properties of a lithographic printing plate obtained according to the DTR-process can be improved by adding a hydrophobic polymer containing mercapto-groups to one or more liquids used for processing an information-wise exposed imaging element to a lithographic printing plate or by treating a lithographic printing plate obtained according to the DTR-process with a finishing liquid or starter solution comprising a polymer containing mercapto-groups so that the hydrophobicity of the obtained silver image is improved.

Hydrophobic polymers for use in accordance with the method of the present invention may be polymers that contain mercapto-groups in the side chain or polymers that are mercapto terminated. Specific examples are mercapto terminated polymers and copolymers of vinyl monomers e.g. acrylate, methacrylate, vinyl chloride, vinylidene chloride, styrenes etc., mercapto terminated epoxy resins, mercapto terminated polysulphides, polysiloxanes having mercapto groups in the side chain etc.. Preferably used are mercapto terminated polysulphides or polysiloxanes having a mercapto group in the side chain.

The mercapto containing polymers used in accordance with the present invention may be prepared using the well known polymerization methods e.g. radical polymerization or polycondensation. Alternatively they may be prepared by polymer modification reactions.

In order to improve the hydrophobicity of the silver image it is essential that the polymers are hydrophobic. By the term "hydrophobic polymer" is meant that said polymers do not dissolve in water i.e. their solubility is lower than 0.05% by weight and preferably lower than 0.01% by weight.

The polymers containing mercapto-groups used in accordance with the present invention are preferably used in the form of a

dispersion or emulsion e.g. in an aqueous processing liquid or in an aqueous finishing liquid. Surfactants used for making said dispersion may be ionic or non-ionic surfactants e.g. a block copolymer of ethylene oxide and propylene oxide, alkylsulphonates, alkylarylsulphonates, alkylaryl substituted ethylene oxides, polyethylenoxides containing an acetylenic group such as surfynol 104, surfynol 465, surfynol 440 etc. all available from Air Reduction Chemical Company New York.. It is important with respect to the present invention that a stable dispersion or emulsion of the mercapto containing polymer is prepared. To obtain a stable dispersion the polymers containing mercapto-groups used in accordance with the present invention are preferably of low molecular weight. For example the weight average molecular weight of the preferably used mercapto terminated polysulphide is preferably between 1000 and 30000 most preferably between 1000 and 10000.

The dispersion of the mercapto-containing polymers according to the present invention may be mixed with dispersion of hydrophobic polymers not containing a mercapto-group. It has indeed been found that the concentration of said polymers containing mercapto groups can be lowered by the addition of a dispersion of another hydrophobic polymer not containing mercapto groups while still maintaining good printing properties. Such offers an ecological advantage. Suitable hydrophobic polymers not containing mercapto groups are e.g. polystyrene, poly(meth)acrylates, polyethylene etc..

The concentration of the mercapto containing polymers used in accordance with the present invention is preferably between 0.05% by weight and 40% by weight most preferably between 0.1% and 30% by weight.

The mercapto containing polymers according to the present invention may be used in combination with low molecular weight hydrophobizing agents e.g. those described in US-P 3,776,728, and US-P 4,563,410. Said low molecular weight hydrophobizing agents may be present in the same liquid that contains the mercapto containing polymers or may be present in another liquid used for obtaining a lithographic printing plate according to the DTR-process.

According to a preferred mode of the present invention a DTR-

imaging element comprising in the order given on an anodized and roughened aluminium support a layer containing physical development nuclei, an optional hydrophilic layer as disclosed in e.g. EP-A-483415 and EP-A-410500 and a silver halide emulsion is information-wise exposed and subsequently developed in the presence of developing agent(s) and silver halide solvent(s). After said development the plate is rinsed with water to remove the silver halide emulsion layer and any other optional layers so that the silver image is exposed. The plate is then preferably treated with a finishing solution comprising a polymer containing mercapto-groups. The concentration of said polymer in said finishing solution is preferably between 0.05% by weight and 20% by weight.

Silver halide developing agents for use in accordance with the present invention are preferably of the p-dihydroxybenzene type, e.g. hydroquinone, methylhydroquinone or chlorohydroquinone, preferably in combination with an auxiliary developing agent being a 1-phenyl-3-pyrazolidinone-type developing agent and/or p-monomethylaminophenol. Particularly useful auxiliary developing agents are of the phenidone type e.g. 1-phenyl-3-pyrazolidinone, 1-phenyl-4-monomethyl-3-pyrazolidinone, and 1-phenyl-4,4-dimethyl-3-pyrazolidinone. However other developing agents can be used. Said developing agents may be contained in an alkaline processing liquid but are preferably contained in one or more layers of the imaging element. In the latter case the alkaline processing liquid merely serves as an alkaline activating liquid.

The pH of said alkaline processing liquid is preferably between 12 and 14 and may be established by an organic and/or inorganic alkali agent. Examples of suitable alkali agents are e.g. sodium hydroxide, carbonates, secondary and/or tertiary alkanolamines, amines etc. or mixtures thereof.

It is furthermore essential that the DTR-process is carried out in the presence of (a) silver halide solvent(s). Said silver halide solvent(s) can be present in one or more layers comprised in the imaging element but are preferably comprised in the alkaline processing liquid. Suitable silver halide solvents for use in accordance with the present invention are e.g. thiosulphate or thiocyanate. Further interesting silver halide complexing agents,

are cyclic imides, preferably combined with alkanolamines, as described in US-P 4,297,430 and US-P 4,355,090 and 2-mercaptobenzoic acid derivatives as described in US-P 4,297,429, preferably combined with alkanolamines or with cyclic imides and alkanolamines.

The alkaline processing liquid preferably also contains a preserving agent having antioxidation activity, e.g. sulphite ions provided e.g. by sodium or potassium sulphite. For example, the aqueous alkaline solution comprises sodium sulphite in an amount ranging from 0.15 to 1.0 mol/l. Further may be present a thickening agent, e.g. hydroxyethylcellulose and carboxymethylcellulose, fog inhibiting agents, e.g. potassium bromide, potassium iodide and a benzotriazole which is known to improve the printing endurance, calcium-sequestering compounds, anti-sludge agents, and hardeners including latent hardeners.

The mercapto containing polymers used in accordance with the present invention may also be added to the alkaline processing liquid in addition to one or more low molecular weight hydrophobizing agents, e.g. those described in US-P 3,776,728, and US-P 4,563,410, that may be present in said processing liquid.

Development acceleration can be accomplished with the aid of various compounds to the alkaline processing liquid and/or one or more layers of the imaging element, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-P 3,038,805 - 4,038,075 - 4,292,400 - 4,975,354.

According to another embodiment of the present invention an imaging element comprising on a support e.g. a paper or resin support in the order given a silver halide emulsion layer and a surface layer containing physical development nuclei is information-wise exposed and developed in the presence of developing agent(s) and silver halide solvent(s) using an alkaline processing liquid as described above. Said development step is preferably followed by a neutralization step using a neutralization liquid to lower the plate surface after development. The mercapto containing polymers used in accordance with the present invention are preferably contained in the neutralization liquid optionally in combination with low molecular weight hydrophobizing agents as described above but may

also be contained in the alkaline processing liquid used for developing the imaging element. The neutralization liquid preferably contains buffer ions, e.g. phosphate buffer or citrate buffer to establish in said liquid a pH value ranging from 5.0 to 7.0. The neutralization solution can further contain bactericides, e.g. phenol, thymol or 5-bromo-5-nitro-1,3-dioxan as described in EP 0,150,517.

The photographic silver halide emulsions used in accordance with the above described imaging elements can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

The photographic silver halide emulsions used according to the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method or the double-jet method.

The silver halide particles of the photographic emulsions used according to the present invention may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

According to the present invention the emulsion or emulsions preferably consist principally of silver chloride while a fraction of silver bromide is present ranging from 1 mole % to 40 mole %. The emulsions may belong to the core/shell type well known to those skilled in the art in the sense that substantially all the bromide is concentrated in the core. This core contains preferably 10 to 40 % of the total silver halide precipitated, while the shell consists preferably of 60 to 90 % of the total silver halide precipitated.

The average size of the silver halide grains may range from

0.10 to 0.70 μm , preferably from 0.25 to 0.45 μm .

The size distribution of the silver halide particles of the photographic emulsions to be used according to the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

Preferably during the precipitation stage Iridium and/or Rhodium containing compounds or a mixture of both are added. The concentration of these added compounds ranges from 10^{-8} to 10^{-3} mole per mole of AgNO_3 , preferably between 10^{-7} and 10^{-6} mole per mole of AgNO_3 . This results in the building in in the silver halide crystal lattice of minor amounts of Iridium and/or Rhodium, so-called Iridium and/or Rhodium dopants. As known to those skilled in the art numerous scientific and patent publications disclose the addition of Iridium or Rhodium containing compounds or compounds containing other elements of Group VIII of the Periodic System during emulsion preparation.

The emulsions can be chemically sensitized e.g. by adding sulphur-containing compounds during the chemical ripening stage e.g. allyl isothiocyanate, allyl thiourea, and sodium thiosulphate. Also reducing agents e.g. the tin compounds described in BE-P 493,464 and 568,687, and polyamines such as diethylene triamine or derivatives of aminomethane-sulphonic acid can be used as chemical sensitizers. Other suitable chemical sensitizers are noble metals and noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium. This method of chemical sensitization has been described in the article of R.KOSLOWSKY, Z. Wiss. Photogr. Photophys. Photochem. 46, 65-72 (1951).

The emulsions of the DTR element can be spectrally sensitized according to the spectral emission of the exposure source for which the DTR element is designed.

Suitable sensitizing dyes for the visible spectral region include methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for this purpose include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes.

Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

The spectral sensitizers can be added to the photographic emulsions in the form of an aqueous solution, a solution in an organic solvent or in the form of a dispersion.

The silver halide emulsions may contain the usual stabilizers e.g. homopolar or salt-like compounds of mercury with aromatic or heterocyclic rings such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, preferably tetra- or penta-azaindenes, especially those substituted with hydroxy or amino groups. Compounds of this kind have been described by BIRR in Z. Wiss. Photogr. Photophys. Photochem. 47, 2-27 (1952). Other suitable stabilizers are i.a. heterocyclic mercapto compounds e.g. phenylmercaptotetrazole, quaternary benzothiazole derivatives, and benzotriazole. Preferred compounds are mercapto substituted pyrimidine derivatives as disclosed in US-P 3,692,527.

The silver halide emulsions may contain pH controlling ingredients. Preferably the emulsion layer is coated at a pH value below the isoelectric point of the gelatin to improve the stability characteristics of the coated layer. Other ingredients such as antifogging agents, development accelerators, wetting agents, and hardening agents for gelatin may be present. The silver halide emulsion layer may comprise light-screening dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes are described in i.a. US-P 4,092,168, US-P 4,311,787, DE-P 2,453,217, and GB-P 1,907,440.

The layer containing physical development nuclei is preferably free of hydrophilic binder but may comprise small amounts upto 30% by weight of the total weight of said layer of a hydrophilic colloid e.g. polyvinyl alcohol to improve the hydrophilicity of the surface. Preferred development nuclei for use in accordance with the present invention are sulphides of heavy metals e.g. sulphides of antimony, bismuth, cadmium, cobalt, lead, nickel, palladium, platinum, silver, and zinc. Other suitable development nuclei are salts such as e.g. selenides, polyselenides, polysulphides, mercaptans, and tin (II) halides. Heavy metals, preferably silver, gold, platinum, palladium,

and mercury can be used in colloidal form. Especially suitable development nuclei in connection with the present invention are palladium sulphide nuclei or metallic silver nuclei.

More details about the imaging elements used in accordance with the present invention and described in the above two embodiments can be found in e.g. EP-A-483415, EP-A-410500, US-P-4.824.760, US-P 4,297,430, US-P 4,355,090, US-P 4,297,429 and EP-A-423399. The invention will now be illustrated by the following examples without however limiting it thereto.

EXAMPLE 1

4 equal imaging elements were made according to the invention sample of example 1 described in EP-A-483415.

The imaging elements were identically exposed through a contact screen in a process-camera and immersed for 8 s at 25°C in a freshly made developing solution (pH=13 (25°C)) having the following ingredients in a CR 430 processor marketed by AGFA-GEVAERT, Belgium:

carboxymethylcellulose	18 g
sodium hydroxide	22.5 g
anhydrous sodium sulphite	120 g
hydroquinone	20 g
1-phenyl-3-pyrazolidinone	3 g
potassium bromide	0.75 g
anhydrous sodium thiosulphate	7.5 g
ethylene diamine tetraacetic acid tetrasodium salt	3.2 g
demineralized water to make	1000 ml

The initiated diffusion transfer was allowed to continue for 30 s to form a silver image on the aluminium foil.

Each of the 4 developed monosheet layer assemblages was then rinsed for 1 min. with a water jet to remove all the layers above the silver image so as to expose it. Both elements were then guided to a finishing solution having the following composition:

10% aqueous n-hexadecyl trimethyl ammonium chloride	25 ml
20% aqueous solution of polystyrene sulphonic acid	100 ml
potassium nitrate	12.5 g
citric acid	20.0 g
1-phenyl-5-mercaptotetrazole	2.0 g
sodium hydroxide	5.5 g
water to make	1000 ml
pH (20°C) = 4	

3 of these elements were respectively wiped with a starter solution 1, 2 and 3 having the following composition:

solution 1:

mercapto polymer 1 (see below)	10%
$p-C_9H_{19}-C_6H_5-O(-CH_2-CH_2O)_{30}H$	1.0%

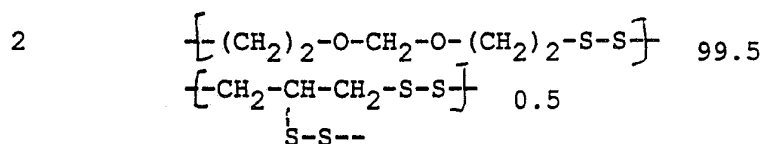
solution 2:

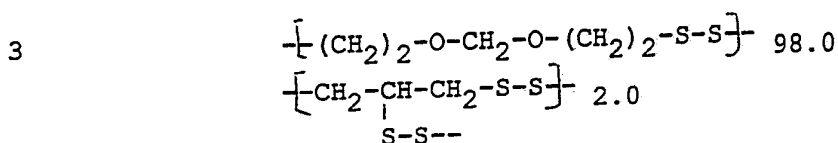
mercapto polymer 2 (see below)	5%
$p-C_9H_{19}-C_6H_5-O(-CH_2-CH_2O)_{30}H$	0.5%

solution 3:

mercapto polymer 3 (see below)	0.6%
$p-C_9H_{19}-C_6H_5-O(-CH_2-CH_2O)_{30}H$	0.5%

Solution number mercapto polymer^{*}





(*) The polymer is represented by its recurring unit(s) and the indices in the above table for polymers 2 and 3 represent the weight % of the branched and non-branched units in these polymers. Polymers 2 and 3 are respectively the polymers LP-32 and LP-3 commercially available from Thiokol Chemicals.

Each of the 4 printing plates obtained was placed on an Heidelberg offset printing press, type GTO, marketed by HEIDELBERGER DRUCKMASCHINEN AG, D-6900 Heidelberg, West-Germany.

Each printing plate was inked with a commercially available KAST + EHINGER 123W ink and then used for printing copy sheets of paper. The results for each of the samples are shown in table 1.

Table 1		
Starter solution	disposed copies *	printing endurance
none	15	75000
1	5	75000
2	5	75000
3	5	100000

(*) number of copies that had to be disposed before a copy of constant quality was obtained.

From the above table 1 it can be seen that the printing characteristics of the plate can be improved using a polymer containing mercapto groups.

EXAMPLE 2

An imaging element as described in example 1 was imaged and processed as described in example 1 with the exception that wiping with a starter solution was omitted and that the finishing solution of example 1 was replaced by a finishing solution of the following

composition:

polymer of starter solution 3 of example 1	2.5%
$\text{p-C}_9\text{H}_{19}\text{-C}_6\text{H}_5\text{-O(-CH}_2\text{-CH}_2\text{O)}_{30}\text{H}$	0.25%
NaOH	1.5%
citric acid	2.3%
NaH_2PO_4	2.3%
KNO_3	1.4%

The thus obtained lithographic printing plate was used to print as described in example 1. 100000 copies of good quality were obtained and only the 5 first copies had to be disposed.

EXAMPLE 3

An imaging element as described in example 1 was imaged and processed as described in example 1 with the exception that a starter solution was used with the following composition:

polymer of starter solution 3 of example 1	0.25%
$\text{p-C}_9\text{H}_{19}\text{-C}_6\text{H}_5\text{-O(-CH}_2\text{-CH}_2\text{O)}_{30}\text{H}$	0.025%
polystyrene	2.5%
polystyrene sulfonic acid	0.25%

The thus obtained printing plate was used to print as described in example 1. 100000 copies of good quality were obtained and only the 5 first copies had to be disposed.

CLAIMS

1. A method for obtaining a lithographic printing plate comprising the steps of:
 - information-wise exposing an imaging element comprising on a support a silver halide emulsion layer and a layer containing physical development nuclei,
 - developing said information-wise exposed imaging element according to the DTR-process in the presence of developing agent(s) and silver halide solvent(s),
 - treating the obtained silver image with a solution containing a hydrophobic polymer comprising mercapto groups.
2. A method according to claim 1 wherein said solution containing said hydrophobic polymer comprising mercapto groups is a developing liquid.
3. A method according to claim 1 wherein said treatment with a solution containing a hydrophobic polymer comprising mercapto groups is carried out after development of said imaging element.
4. A method according to any of claims 1 to 3 wherein said hydrophobic polymer containing mercapto groups is a mercapto terminated hydrophobic polymer.
5. A method according to any of claims 1 to 3 wherein said hydrophobic polymer containing mercapto groups is a hydrophobic polymer containing mercapto groups in the side chain.
6. A method according to claim 4 wherein said hydrophobic polymer is a mercapto terminated polysulphide.
7. A method according to 5 wherein said hydrophobic polymer is a polysiloxane containing mercapto groups in the side chain.

8. A method according to claims 6 or 7 wherein said hydrophobic polymer containing mercapto groups has a weight average molecular weight between 1000g/mol and 30000g/mol.

9. A method according to any of the above claims wherein said solution containing said hydrophobic polymer containing mercapto groups further contains a hydrophobic polymer not containing mercapto groups.

10. A method according to any of the above claims wherein said hydrophobic polymer containing mercapto groups is contained in said solution in an amount between 0.05% by weight and 40% by weight.

INTERNATIONAL SEARCH REPORT

PCT/EP 92/02590

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 G03F7/07

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	G03F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	DE,B,1 622 743 (AGFA-GEVAERT AKTIENGESELLSCHAFT) 3 June 1971 see column 4, line 18 - line 42 ---	1-4
Y	RESEARCH DISCLOSURE. no. 161, September 1977, HAVANT GB pages 23 - 24 R.J.KEMP ET AL 'Lithographic printing plates' see page 23, right column, paragraph 6 ---	1-5
Y	US,A,3 161 508 (M.HEPHER ET AL) 15 December 1964 see column 2, line 25 - column 3, line 65 ---	1-5
A	US,A,4 160 670 (Y.TSUBAI) 10 July 1979 see the whole document ---	6-10
	--- -/--	

¹⁰ Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 16 DECEMBER 1992	Date of Mailing of this International Search Report 30. 12. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer BOLGER W.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>DATABASE WPIL Week 8107, Derwent Publications Ltd., London, GB; AN 81-10378D & JP,A,55 098 753 (MITSUBISHI PAPER MILLS LTD) 29 July 1980 see abstract</p> <p>-----</p>	6-10

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

EP 9202590
SA 66288

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 16/12/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
DE-B-1622743	03-06-71	BE-A-	615823	
		CH-A-	423477	
		FR-A-	1321685	
		GB-A-	969072	
		NL-A-	276634	

US-A-3161508		BE-A-	582160	
		BE-A-	582161	
		FR-A-	1242943	
		FR-A-	1243430	
		GB-A-	934691	
		GB-A-	934692	
		GB-A-	934693	
US-A-4160670	10-07-79	JP-C-	1081155	29-01-82
		JP-A-	53021602	28-02-78
		JP-B-	56024262	04-06-81
		DE-A, C	2735381	16-02-78
