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(54) **Fountain solution for a diazobased lithographic printing plate.**

(57) The present invention provides a fountain solution for a diazo-based lithographic printing plate comprising a dextran whereof at least part of the hydroxyl groups have been modified into an amine and/or ammonium containing organic residue. The fountain solution preferably also contains hexylene glycol. Scumming and ink staining of diazo-based lithographic printing plates developed by plain water is avoided.

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1. Field of the invention.

The present invention relates to method for printing with a diazo-based lithographic printing plate and to a fountain solution for use in said method.

2. Background of the invention.

Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

In the art of photolithography, a photographic material is made image-wise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophillic background.

In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophillic colloids and a large variety of synthetic photopolymers.

Particularly diazo-sensitized systems are widely used. These systems have been extensively reviewed by Kosar J. in "Light-Sensitive Systems", Wiley, New York, 1965, Chapter 7.

A generally used negative-working diazo-sensitized system is based on the capability of diazo compounds to harden a polymer when exposed to ultraviolet and blue radiation. Diazo compounds which have been used for the preparation of lithographic printing plates based on their hardening properties are e.g. diazonium salts whose photolysis products can harden polymers (natural colloids or synthetic resins) directly and diazonium polymers. Although polymers containing diazonium groups have a large structure they may remain water soluble owing to the presence of the ionic diazonium groups. When these groups are destroyed by exposure to light an insoluble resin is formed.

During a development step subsequent to the information-wise exposure the diazo resin or diazonium salt will be dissolved and removed by a suitable solvent, e.g. water, in the non-exposed or insufficient exposed parts of the lithographic printing plate precursor. The hydrophillic or oleophobic surface of the plate will thus be exposed in the non-exposed or insufficient exposed parts while the oleophillic diazo resin will remain in the exposed parts.

Several types of supports can be used for the manufacturing of a diazo-sensitized lithographic printing plate. Common supports are metal supports like Al or Zn.

Other supports that are employed are polyester film supports and paper supports coated with a hydrophillic layer to form the hydrophillic background of the printing plate. A typical hydrophillic layer in these systems is a layer containing polyvinyl alcohol and hydrolyzed tetraethyl orthosilicate and preferably also silicium dioxide and/or titanium dioxide as described in e.g. GB-P-1419512, FR-P-2300354, US-P-3971660 and 4284705.

During the printing operation such printing plates, which carry a line or dot image, need to be moistened with a fountain liquid so as to wet the non-image areas of the printing plates and consequently prevent printing ink from depositing in these non-image areas. A deposit of ink in the non-image areas, however slight it may be, impairs the print quality. This problem is known as staining or scumming and appears especially with diazo-based lithographic printing plates of the type described in e.g. US-P-3971660 or EP-A-90200801.0 developed with plain water. The type of staining and/or scumming that occurs with the latter type of lithographic printing plates is probably due to diazo remaining in the non-image areas.

To avoid staining and scumming several types of additives can be added to the fountain solution. For example it is known to add hydrophillic substances such as e.g. arabic gum, cellulose derivatives, polyvinyl alcohol, polyvinyl pyrrolidone etc. to improve the hydrophillicity of the background. See for example DE 2.653.824 and EP-A-249751. Other additives commonly used in fountain solutions are alcohols e.g. isopropanol, ethyleneglycol, glycol ether, polyols, 3-hydroxymethyl-4-heptanol.

However the fountain solutions described in the prior art are not satisfactory with respect to staining and/or scumming encounterred with diazo-based lithographic printing plates especially the diazo-based lithographic printing plates described in US-P-3971660 or EP-A-90200801.0 when developed with plain water.

3. Summary of the invention.

It is an object of the present invention to solve the problem of ink staining and/or scumming encounterred with diazo-based lithographic printing plates.

Other objects will become clear from the description hereinafter.

According to the present invention there is provided a fountain solution comprising a dextran of which at least part of the hydroxyl groups have been modified into groups containing ammonium groups and/or amine functions.

According to the present invention there is also provided a method for printing with a diazo-based lithographic printing plate using a fountain solution comprising a dextran of which at least part of the hydroxyl groups have been modified into groups containing ammonium groups and/or amine functions.

4. Detailed description of the invention.

It has been found that the scumming and ink staining of a diazo-based lithographic printing plate can be reduced by using a fountain solution comprising a dextran of which at least part of the hydroxyl groups have been modified into groups containing ammonium groups or amine functions. Said dextran preferably has a molecular weight between 10000 and 500000.

Preferably used dextrans of which at least part of the hydroxyl groups have been modified into groups containing ammonium groups or amine functions are dextrans of which at least some of the hydroxyl groups have been modified into one or more of the following groups:

-O-R^1
-O-CO-R^2

wherein R^1 represents an organic residue containing an ammonium group or an amine function, e.g. an amine or ammonium substituted alkyl, an amine or ammonium substituted alkylaryl etc..
R^2 has one of the significances given for R^1 or stands for -OR^3 or -$N(R^4)R^5$, wherein R^3 has one of the significances given for R^1 and each of R^4 and R^5 which may be the same or different represents hydrogen, an organic group e.g. an alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, an alkylaryl group, an organic residue containing an amine function or ammonium group.

Examples of dextrans suitable for use in accordance with the present invention are dextrans wherein some of the hydroxyl groups have been modified into one of the groups shown in table 1.

Table 1

Compound no.	modified group
1	-O-CH_2-CH_2-NH_2
2	-O-CO-NH-CH_2-CH_2-NH_2
3	-O-CO-NH-CH_2-CH_2-$N(CH_2$-CH_2-$NH_2)_2$
4	-O-CH_2-CH_2-NH-CH_2-CH_2-NH_2
5	-O-CH_2-CH_2-NH-CH_2-CHOH-CH_2-$N^+(CH_3)_3$ Cl^-
6	-O-$(CH_2$-CH_2-O$)_n$-CH_2-CH_2-NH_2 wherein n represents an integer from 1 to 50
7	-O-CO-NH-CH_2-CH_2-NH-CH_2-CHOH-CH_2-$N^+(CH_3)_3$ Cl^-
8	-O-CH_2-CH_2-$N(CH_2$-CH_2-$NH_2)_2$
9	-O-CONH-CH_2-CH_2-$N(CH_2$-CH_2-$NH_2)_2$
10	-O-CONH-$(CH_2$-CH_2-O$)_n$-CH_2-CH_2-NH_2 n having the same meaning as defined above

The modified dextrans can be prepared by reaction of a dextran with e.g. alkylating agents, acid halides, chloroformates, carboxylic acids etc...

The dextrans are preferably used in a total amount between 0.025g/l and 0.5g/l in the fountain solution as used on a printing machine.

In addition to the dextrans the fountain solution for use in accordance with the present invention preferably also comprises a glycol preferably in an amount from 0.1g/l to 80g/l. Examples of glycols

suitable for use in accordance with the present invention are e.g. ethylene glycol, propylene glycol, glycol ether, hexylene glycol etc. Hexylene glycol is most preferably used in accordance with the present invention.

The pH of the fountain solution for use in accordance with the present invention is preferably between 4 and 7. The fountain solution is preferably bufferred around the desired pH using a suitable buffer. Buffers that can be used in accordance with the present invention are e.g. citrate buffers, acetate buffers, phosphate buffers etc. or mixtures thereof.

It may also be desirable to incorporate other additives such as e.g. hydrophillic colloid binders, organic and inorganic acids e.g. hydrogen chloride, preservatives, corrosion inhibitors, and hardeners into the fountain liquid. Such additives can be used in amounts of from about 0.01 to about 5 percent by volume.

According to the method of the present invention a diazo-based lithographic printing plate prepared as described in e.g. US-P-3971660 or EP-A-90200801.0 is moistened with the above described fountain solution, supplied with ink and used to print on an offset press. Suitable inks for use in accordance with the printing method of the present invention are those inks commonly employed in the art of lithographic printing.

The following examples illustrate the present invention without limiting it thereto. All parts are by weight unless otherwise stated.

EXAMPLE 1 (comparitive)

A comparitive fountain solution consisting of 10% of isopropanol in water was prepared.

A lithographic printing plate prepared as described in EP-A-90200801.0 was mounted on an Heidelberg GTO 46 offset printing press with a dampening system adapted for alcoholic fountain solutions comprising the above described fountain solution. The ink used was Van Son rubberbase 2329 commercially available from Van Son.

During printing scumming was noticed in the non-image parts of the plate especially those parts that have been exposed to daylight after the information-wise exposure and development of the plate.

EXAMPLE 2 (comparitive)

A lithographic printing plate prepared as described in example 1 was used to print under identical conditions as in example 1 with the exception that an aqueous fountain solution having the following composition was used:

isopropanol	10%
hexylene glycol	4%

Ink staining occurred in the non-image parts of the plate especially those parts that have been exposed to daylight after information-wise exposure and development of the plate.

EXAMPLE 3

A lithographic printing plate prepared as described in example 1 was used to print under similar conditions as in example 1 with the exception that an aqueous fountain solution having the following composition was used:

isopropanol 10%
Dormacid* 0.25%
* Dormacid is commercially available from Pfeifer & Langen and is the commercial name for a dextran modified with group 8 of table 1 above.

The water supply was set to position 7 at the printing machine for a density of 1.5 at ink supply 15. No

scumming nor ink staining was noticed.

EXAMPLE 4

A lithographic printing plate prepared as described in example 1 was used to print under similar conditions as in example 1 with the exception that an aqueous fountain solution having the following composition was used:

isopropanol	10%
hexylene glycol	4%
Dormacid*	0.25%

* Dormacid is commercially available from Pfeifer & Langen and is the commercial name for a dextran modified with group 8 of table 1 above.

The water supply was set to position 5 at the printing machine (less water supply than in example 3) for a density of 1.5 at ink supply 15. No scumming nor ink staining was noticed. The fountain solution of this example thus offers the best results since no scumming nor ink staining occurs and since the water supply is less than in example 3 offers more flexibility at the offset press.

Claims

1. A fountain solution comprising a dextran whereof at least part of the hydroxyl groups have been modified into an amine and/or ammonium containing organic residue.

2. A fountain solution according to claim 1 wherein said dextran is a dextran whereof at least part of the hydroxyl groups have been modified into one or more of the following groups:

   $-O-R^1$
   $-O-CO-R^2$

   wherein R^1 represents an organic residue containing an ammonium group or an amine function, R^2 has one of the significances given for R^1 or stands for $-OR^3$ or $-N(R^4)R^5$, wherein R^3 has one of the significances given for R^1 and each of R^4 and R^5 which may be the same or different represents hydrogen or an organic residue.

3. A fountain solution according to claim 1 or 2 wherein said fountain solution also comprises a glycol.

4. A fountain solution according to claim 3 wherein said glycol is hexylene glycol.

5. A fountain solution according to any of claims 1 to 4 wherein said dextran is used in a concentration between 0.025g/l and 0.50g/l.

6. A method for printing with a diazo-based lithographic printing plate comprising the steps of moistening the diazo-based lithographic printing plate with a fountain solution as defined in any of claims 1 to 5 and supplying ink to said diazo-based lithographic printing plate.

7. A method according to claim 6 wherein said diazo-based lithographic printing plate was obtained by developing with plain water an information-wise exposed imaging element comprising on a polyester film support a hydrophillic layer comprising polyvinyl alcohol hardened with tetraalkyl orthosilicate and a layer containing a diazo resin or diazonium salt.

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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 1423

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-2 648 805 (SUMITIOMO CHEMICAL)		B41N3/08
A	EP-A-0 192 813 (FIRMA CARL FREUDENBERG)		
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 40 (M-278)(1477) 21 February 1984 & JP-A-58 197 091 (KONISHIROKU SHASHIN KOGYO KK) * abstract *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B41N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 FEBRUARY 1992	HAENISCH U.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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