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(54) A method for stabilizing heat sensitive elements, developable by an aqueous solution

(57) According to the present invention there is provided a method to obtain a good shelf life of a heat sensitive imaging element, developable by an aqueous solution by introducing a moisture regulating member in a packaging of said elements whereby the amount of water in the imaging element is reduced to a level corresponding to an equilibrium moisture content below 65.5 % R.H. at 50°C.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method for obtaining a good shelf life of heat sensitive elements, developable by an aqueous solution. The present invention especially relates to the use of interleaves in the packaging of said heat sensitive elements.

BACKGROUND OF THE INVENTION.

[0002] 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.
[0003] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy ink in the photo-exposed (negative working) or in the non-exposed areas (positive working) on a hydrophilic background.
[0004] In the production of common lithographic 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 hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.
[0005] Upon imagewise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.
[0006] On the other hand, methods are known for making printing plates involving the use of imaging elements that are heat sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat sensitive printing plate precursors is clearly seen on the market.
[0007] For example, **Research Disclosure no. 33303 of January 1992** discloses a heat sensitive imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.
[0008] EP-A- 800 928 discloses a heat sensitive imaging element comprising on a hydrophilic surface of a lithographic base an image forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a water insoluble alkali soluble or swellable resin and a compound capable of converting light into heat, said compound being present in said image forming layer or a layer adjacent thereto, wherein said alkali swellable or soluble resin comprises phenolic hydroxy groups and/or carboxyl groups. However by exposure with short pixel times of said heat-sensitive imaging element there occurs ablation on the exposed areas resulting in an insufficient ink acceptance.
[0009] Analogous imaging elements comprising on a hydrophilic surface of a lithographic base an image forming layer comprising hydrophobic thermoplastic polymer particles dispersed in a water or alkali soluble or swellable resin and a compound capable of converting light into heat, said compound being present in said image forming layer or a layer adjacent thereto are disclosed in e.g. **EP-A- 770 494, EP-A- 770 495, EP-A- 770 496, EP-A- 770 497, EP-A- 773 112, EP-A- 773 113, EP-A- 774 364, EP-A- 800 928, EP-A- 832 739, EP-A- 839 647, EP-A- 839 648 and EP-A- 849 091**. In most of these applications poly(meth)acrylate latices are used as thermoplastic polymer particles and no specific hydrophilic resin is mentioned In most cases carbon black or an IR-dye are mentioned as the compound capable of converting light into heat.
[0010] In order to prepare an imaging element as described above, that is processable on the press, preferably IR-dyes should be used. Carbon black causes indeed a soiling on the press when removing the unexposed areas.
[0011] The shelf life of these elements is nowhere discussed in the litterature. Still, on press processable printing plates are very sensitive to water and to water vapour. This is a consequence of the fact that these plates should be processable in an aqueous medium, being it in a one-phase medium, when a suitable fountain is used. On the other hand the ink-water emulsion of the printing process can act as developing medium. Also in this system the aqueous phase will have an important influence in the developing process.
[0012] It is inevitable that the heat sensitive coating contains a certain amount of water during the drying process

and further during the preservation. If this water becomes already active during the preservation of the material this will result in a deteriorating of the properties of the material. Therefore these materials should be dried and packed at a very dry condition. This is impossible in practice. The drying of production rooms is very expensive and ask a lot of effort to guarantee the stability in function of the time. Furtheron there originates problems of dust attraction and electrostatic problems.

[0013] Usually the shelf life of a material is determined by subjecting the material during a short time to a certain temperature to make it possible to make predictions on a long term. Hereby is a standard test: packing the material moistureproof at a temperature treatment of 50°C. A good shelf life is defined when the material endures a period of 3 days without considerable deterioration of the product properties.

[0014] It has been found that heat sensitive materials, developable in an aqueous medium do not withstand this test when they are packed at 25% R.H. at 20°C, it is to say at very dry conditions. So, a method to improve the shelf life of said materials is very desirable.

OBJECTS OF THE INVENTION.

[0015] It is an object of the present invention to provide a method to improve the shelf life of heat sensitive imaging elements which are developable in an aqueous medium.
Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION.

[0016] According to the present invention there is provided a method to obtain a good shelf life of a heat sensitive imaging element, developable by an aqueous solution by introducing a moisture regulating member in a packaging of said elements whereby the amount of water in the imaging element is reduced to a level corresponding to an equilibrium moisture content below 65.5 % R.H. at 50°C.

DETAILED DESCRIPTION OF THE INVENTION.

[0017] It has been found that lithographic printing plates of high quality with a good shelf life can be obtained according to the method of the present invention.. More precisely it has been found that the packaged material should fulfill the following equation:

$$[MC]^{22} \leq [MC]^{50}_{MAX}$$

where

$$[MC]^{22} = \sum_{n}^{22} [(a_n \times RH_n + b_n) \times d_n]$$

and

$$[MC]^{50}_{MAX} = \sum_{n}^{50} [(a_n \times 65.5 + b_n) \times d_n]$$

$[MC]^t_L$ moisture content in g/m^2 at temperature t.

d_L thickness of element, expressed in g/m^2.

t temperature in °C.
L element (imaging or absorbing).

a_L slope: curve moisture content vs RH expressed in 1/% RH.

RH_L corresponding equilibrium relative humidity expressed in % RH.

b_L intercept: curve moisture content vs RH, dimensionessless.

[0018] Preferably, to fulfill the goal of the invention a moisture accepting sheet is used in the packaging of said material. Preferably said sheet material is paper or paperlike material which can be coated. Suitable paper is e.g.H + E 36 g, H + E 40 g, Intermills 60 g. Other suitable sheet material is plastic or coated plastic. The sheet material can also be from inorganic nature, glass or ceramic.
[0019] In another preferred mode the absorbing element is a backing coating on the imaging element.
[0020] The pile of heat sensitive elements with intermediate sheets is preferably packed in a polyethylene-aluminum-paper laminate with the paper side being the outside of the packaging material.
[0021] A preferred imaging element comprises on a lithographic base with a hydrophilic surface an image forming layer including thermoplastic particles of a homopolymer or a copolymer of styrene and a hydrophilic polymer containing carboxyl groups, wherein said imaging element further contains an anionic IR-cyanine dye being present in said image forming layer or a layer adjacent thereto, Such heat sensitive imaging elements are described with their exposure and development in **EP-A- 98 200 187**.
[0022] The lithographic base is preferably an anodized roughned aluminum support but a flexible support coated with a hydrophilic hardened layer can also be used.
[0023] The imaging element can after exposure to an IR-laser be developed by rinsing the element with an aqueous solution. Preferably the exposed imaging element is mounted directly on the press.
[0024] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

Examples

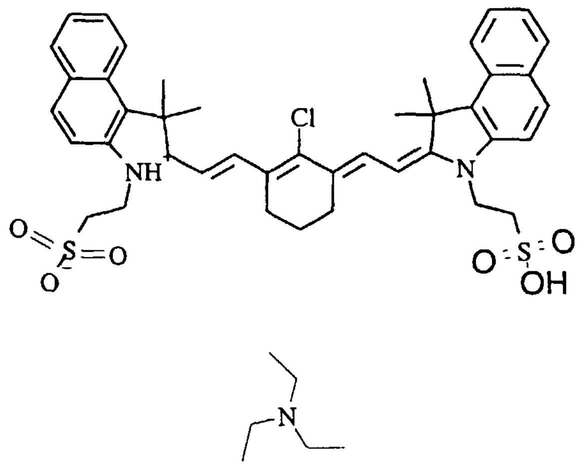
Comparative Example 1

Preparation of the lithographic base

[0025] A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 to form a surface topography with an average center-line roughness Ra of 1.1 µm.
[0026] After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.
[0027] The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m^2 for about 300 seconds to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3 then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and subsequently with a solution containing aluminum trichloride, rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the heat-mode imaging element

[0028] On above mentioned lithographic base, was coated a layer from an 2.61% wt solution in water, with a wet coating thickness of 30µm. The resulting layer contained 75% W/W of polystyrene latex, 10 % of a heat absorbing compound, presented in formula (I), 15% W/W of Glascol E15, additionally 6 mg/m^2 of a fluorosurfactant was added. This layer was dried on a temperature of 60°C for at least 42 seconds.
Glascol E15 is a polyacrylic acid, commercial available at N.V. Allied Colloids Belgium. The heat absorbing compound is represented by formula I.



Formula (I)

Preparation imaging element for shelf life testing

[0029] The imaging element was conditioned at 15% RH at 22°C during at least 12 h. Then a pile of 20 plates was put together in a moisture proof package consisting of a polyethylene - aluminium - paper laminate. The outside of the packaging material was the paper side. Also the packaging material was preconditioned during at least 24 h at the same environmental condition.

Comparative example 2

[0030] The same base and heat-mode imaging element was used as described in comparative example 1.

Preparation imaging element for shelf life testing

[0031] The same procedure was used as described in comparative example 1 however the environmental condition was 25% RH at 22°C.

Example 3

[0032] The same base and heat-mode imaging element was used as described in comparative example 1.

Preparation imaging element for shelf life testing

[0033] Both the imaging element and an interleave paper of 36 g/m^2 was conditioned at 22°C/30% RH during at least 12h. Then a pile of 20 plates was put together with between each plate a preconditioned interleave paper in a moisture proof package consisting of a polyethylene - aluminium - paper laminate. The outside of the packaging material was the paper side. Also the packaging material was preconditioned during at least 24 h at the same environmental condition.
The used interleave paper is commercial available at Hoffmann und Engelmann, Neustadt - Weinstraße, Germany.

Example 4

[0034] The same base and heat-mode imaging element was used as described in comparative example 1.

Preparation imaging element for shelf life testing

[0035] Both the imaging element and an interleave paper of 36 g/m^2 was conditioned at 22°C/40% RH during at least 12h. Then a pile of 20 plates was put together with between each plate a preconditioned interleave paper in a

moisture proof package as described in former examples.
The used interleave paper is commercial available at Hoffmann und Engelmann, Neustadt - Weinstraße, Germany.

Example 5

[0036] The same base and heat-mode imaging element was used as described in comparative example 1.

Preparation imaging element for shelf life testing

[0037] Both the imaging element and an interleave paper of 36 g/m^2 was conditioned at 22°C/45% RH during at least 12h. Then a pile of 20 plates was put together with between each plate a preconditioned interleave paper in a moisture proof package consisting as described above.
The used interleave paper is commercial available at Hoffmann und Engelmann, Neustadt - Weinstraße, Germany.

Example 6

[0038] The same base and heat-mode imaging element was used as described in comparative example 1.

Preparation imaging element for shelf life testing

[0039] The imaging element was conditioned at 22°C/60% RH during at least 12h.
On the other hand, the interleave paper was preconditioned at 40% RH at 22°C during at least 12h. Then a pile of 20 plates was put together with between each plate a preconditioned interleave paper in a moisture proof package as described above. This stapling of the materials was carried out as fast as possible, trying to limite the moisture exchange with the environment.
The packaging material was preconditioned during at least 24 h at 60% RH at 22 °C.
The used interleave paper is commercial available at Hoffmann und Engelmann, Neustadt - Weinstraße, Germany.

Determination of moisture content

[0040] In a Cahn-type balans apparatus with installed dew point measurement system, the moisture content of both the imaging element and absorbing material is determined. The used type of instrument is a SGA100 model, commercially available at VTI Corporation, Florida. A strip of the testing material was placed in the balans and dried at 50°C-1%RH till equilibrium. Then the humidity was increased in steps of 10% RH untill state of equilibrium before setting the next step. The increase in weight was registrated.
For the absorption isotherm at room temperature, the same procedure for nulling was made; drying at 50°C-1%RH till equilibrium. This point was set to zero weight. Then the sample was cooled down to 22°C followed by the different increments in RH, every time till equilibrium.
The data are graphically presented as amount of water per unit of area and in the zone 30-60 RH, the absorption seems to be very linear. Following equation can be presented for both the imaging element and the absorbing material:
[0041] For the ease of calculation by using different coating weights or thicknesses from absorbing materials, an equation can be formulated, corresponding to a well defined temperature as follows:
[0042] Total moisture content of the element:

$$[MC]_L^t = [MCs]_L^t \times dL$$

$[MC]_L^t$	moisture content in g/m^2 at temperature t.
$[MCs]_L^t$	specific moisture content as unity of thickness at temperature t, this means moisture content for a hypothetic thickness of 1 g/m^2 of the element. This is a dimensionesless parameter.
dL	thickness of element, expressed in g/m^2.
t	temperature in °C.
L	element (imaging or absorbing).

[0043] Specific moisture content of the element:

$$[MCs]_L^t = [(aL \times RH + bL)]$$

a_L slope: curve moisture content vs RH expressed in 1/% RH.
RH_L corresponding equilibrium relative humidity expressed in % RH.
b_L intercept: curve moisture content vs RH, dimensionessless.

[0044] In above described experiments following values are obtained for a and b:

		Imaging element	Absorbing element
	d_L	0.785 g/m^2	36.0 g/m^2
22 °C	a_L	0.3949 10-3	0.7333 10-3
	b_L	5.4777 10-3	20.5111 10-3
50 °C	a_L	0.3439 10-3	0.8583 10-3
	b_L	-7.5159 10-3	1.3083 10-3

Results of moisture content measurements:

[0045] Following calculations need to be made for prediction of shelf life:
[0046] Maximum acceptable moisture content at 50°C to obtain good shelf life:
In the case of no use of moisture regulating element:

$$[MC]^{50}_{MAX} = [(aIM \times 65.5 + bIM) \times dIM]$$

[0047] In the case of use of moisture regluating element:

$$[MC]^{50}_{MAX} = [(aIL \times 65.5 + bIL) \times dIL] + [(aIM \times 65.5 + bIM) \times dIM]$$

[0048] Moisture content at room temperature at packaging time of the materials:

$$[MC]^{22} = [(aIL \times RHIL + bIL) \times dIL] + [(aIM \times RHIM + bIM) \times dIM]$$

RH_{IL}: Equilibrium moisture content of imaging element at the moment of packaging.
RH_{IM}: Equilibrium moisture content of absorbing element at the moment of packaging.

	g/m^2 water
$[MC]^{50}_{MAY}$ without moisture regulating element	0.0118
$[MC]^{50}_{MAY}$ with moisture regulating element from example 3	1.9886
Comparative example 1	0.0114
Comparative example 2	0.1535
Example 3	1.5440
Example 4	1.8111
Example 5	1.998
Example 6	1.8173

[0049] Above mentioned equations can be more generally expressed as following if more than 2 different materials are included in the packaging:

$$MC^{t} = \sum_{n}^{t} \left[\left([MCs]_{n}\right) \times d_{n}\right]$$

$[MC]^t$	total moisture content in g/m^2 at temperature t.
$[MCs]_n^t$	specific moisture content as unity of thickness at temperature t, this means moisture content for a hypothetic thickness of 1 g/m^2 of the element. This is a dimensionesless parameter.
dn	thickness of the element, expressed in g/m^2.
t	temperature in °C.
n	element.

Determination of Shelf Life:

[0050] The above mentioned packages were placed for different times both at 50°C and as a reference on 22°C. After determined times the above mentioned materials were imaged on a Creo 3244TTM external drum platesetter at 2400 dpi at 150 rpm with a power setting of 15,5 Watt. The imaged plates were printed on a GTO46 printing machine with a K+E 800 Skinnex ink and fountain Rotamatic.
The prints were inspected concerning image quality and quotated. The staining behaviour of the different materials is evaluated. This material property is concerned as the most critical parameter in respect to shelf life.

Results shelf life

[0051] In following table, the summary of the test evaluations at 50°C is presented. The time threatment at 50°C, still resulting in good material characteristics is presented.

Example	Staining behaviour OK	Shelf life
Comparative 1	> 10 days 50°C	OK
Comparative 2	1 day	not OK
3	> 10 days	OK
4	> 10 days	OK
5	2 days	not OK
6	> 10 days	OK

[0052] It is clear from said results that the use of dry interleave paper markedly improves the shelf life of a heat sensitive element, that is developable with water.

Claims

1. A method to obtain a good shelf life of a heat sensitive imaging element, developable by an aqueous solution by introducing a moisture regulating member in a packaging of said elements whereby the amount of water in the imaging element is reduced to a level corresponding to an equilibrium moisture content below 65.5 % R.H. at 50°C.

2. A method according to claim 1 wherein the packaged material fulfills following equation:

$$[MC]^{22} \leq [MC]^{50}_{MAX}$$

where

$$[MC]^{22} = \sum_{n}^{22} [(a_n \times RH_n + b_n) \times d_n]$$

and

$$[MC]_{MAX}^{50} = \sum_{n}^{50} [(a_n \times 65.5 + b_n) \times d_n]$$

$[MC]_L^t$ moisture content in g/m^2 at temperature t.
d_L thickness of element, expressed in g/m^2.

t temperature in °C.
L element (imaging or absorbing).

a_L slope: curve moisture content vs RH expressed in 1/% RH.
RH_L corresponding equilibrium relative humidity expressed in % RH.
b_L intercept: curve moisture content vs RH, dimensionessless.

3. A method according to claim 1 or 2 wherein at least one part of the moisture regulating element is a sheet material.

4. A method according to claim 1 to 3 wherein the sheet material is paper or paperlike material which may be coated.

5. A method according to any of claims 1 to 3 wherein the sheet material is a plastic or coated plastic.

6. A method according to any of claims 1 to 3 wherein the sheet material is from inorganic nature, glass or ceramic.

7. A method according to any of claims 1 to 3 wherein the sheet material is a backing coating on the imaging element.

8. A method according to any of claims 1 to 7 wherein the imaging element comprises thermoplastic polymer particles.

9. A method according to any of claims 1 to 8 wherein the imaging element is coated on an anodised roughned aluminium support.

10. A method according to any of claims 1 to 9 wherein the imaging element is imaged and directly printed on press without additional processing in between.

11. A packaged material comprising at least one heat sensitive imaging element , developable by an aqueous solution comprising a moisture regulating member whereby the amount of water in the imaging element is reduced to a level corresponding to an equilibrium moisture content below 65.5 % R.H. at 50°C.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2645

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.7)
X	US 4 680 248 A (ROACH DONALD J) 14 July 1987 (1987-07-14) * column 2, line 16 - line 48 * * column 3, line 15 - line 41 * * examples *	1	B65D81/26
Y		3-10	
X	US 3 730 334 A (TSUJI A) 1 May 1973 (1973-05-01) * claims *	11	
Y		3-10	
X	EP 0 872 768 A (ORIENTAL PHOTO IND CO LTD) 21 October 1998 (1998-10-21) * page 2, line 46 - line 51 * * page 3, line 10 * * claims * * examples *	11	
A	US 4 965 165 A (SACCOCIO EDWARD J ET AL) 23 October 1990 (1990-10-23) * column 2 * * column 3, line 42 - line 51 * * claims *	1-11	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
B41C
G03F
G03C
B65D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 December 1999	Martins Lopes, L

CATEGORY OF CITED DOCUMENTS

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