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(54) **A method for making positive working printing plates from a latex**

(57) According to the present invention there is provided a method for making a lithographic printing plate comprising the steps of dispensing in a predetermined pattern a synthetic latex of particles of a hydrophobic polymer onto a hydrophilic surface of a lithographic base and heating said lithographic base to at least the glass transition temperature (T_g) of the hydrophobic polymer.

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Description

FIELD OF THE INVENTION

5 [0001] The present invention relates to methods for making lithographic printing plates. In particular, it relates to a method for directly making the lithographic printing plates by using hydrophobic polymer latex printing, which makes it possible to produce the lithographic plates directly from digital data output from computers, facsimiles, or the like without using any films having negative or positive images.

10 BACKGROUND OF THE INVENTION.

[0002] Digitalization of information has made a rapid progress in recent years throughout the process from manufacturing a block copy, an upper stream process of printing, to manufacturing a printing plate, thereby putting to practical use for example, a photographic form system of characters, by which a block copy of manuscripts can be readily prepared, or a scanner which directly reads picture images. With this progress, there has arisen a demand for a direct plate-making method in which lithographic plates can be directly prepared from digital data output from computers, facsimiles, or the like without using a film for making printing plates.

[0003] As one example of the direct plate-making method, a method wherein an image or non-image portion is directly formed on a substrate by ink-jet printing is known to the art. The ink-jet printing system is a relatively rapid image output system and has a simple construction because it does not require any complex optical system. Therefore, the printing system makes an apparatus for making printing plates simple and the cost for making printing plates can be reduced since the maintenance labor is largely reduced.

[0004] As examples of the methods for preparing printing plates by using the ink-jet printing system, Japanese Kokai Publication 113456/1981 proposes the methods for preparing printing plates wherein ink-repelling materials (e.g. curable silicone) are printed on a printing plate by ink-jet printing. The printing plate obtained by this method is an intaglio printing plate in which the ink-repelling material formed on the surface of the substrate serves as a non-image part. As a result, the resolution of the printed images at shadow area or reversed lines is not so good. Moreover, a large amount of ink is needed in this method because the ink-repelling material must be deposited on the whole non-image part which occupies most of the surface of the printing plate, thereby delaying the printing process.

30 [0005] US-P- 5 511 477 discloses a method for the production of photopolymeric relief-type printing plates comprising: forming a positive or a negative image on a substrate by ink-jet printing with a photopolymeric ink composition, optionally preheated to a temperature of about 30°-260°C; and subjecting the resulting printed substrate to UV radiation, thereby curing said ink composition forming said image. This is an obnoxious method due to the sometimes high vapour pressure and toxicity of said inks.

35 [0006] US-P- 5 312 654 discloses a method for making lithographic printing plates comprising: forming an image on a substrate having an ink absorbing layer and a hydrophilized layer between the substrate and absorbing layer by ink-jet printing using a photopolymerizable ink composition, and exposing it to an active light in the wavelength region with which said ink composition is sensitized to cure the image. The printing endurance of said printing plates is low.

40 [0007] Japanese Kokai Publication 69244/1992 discloses a method for making printing plates comprising the steps of forming a printed image on a recording material subjected to a hydrophilic treatment by ink-jet printing using a hydrophobic ink containing photocurable components; and exposing the whole surface to an active light. However, the surface of the substrate to be used for the lithographic plate is usually subjected to various treatments such as a mechanical graining, an anodizing or a hydrophilic treatment to obtain good hydrophilic property and water retention property. Therefore, even the use of an ink composition having a very high surface tension results in a poor image on the surface of the substrate because of ink spreading and low printing endurance.

45 [0008] EP-A- 533 168 discloses a method for avoiding said ink spreading by coating the lithographic base with an ink absorbing layer which is removed after ink printing. This is an uneconomical and cumbersome method.

[0009] Research Disclosure 289118 of May 1988 discloses a method for making printing plates with the use of an ink jet wherein the ink is a hydrophobic polymer latex. However said printing plates have a bad ink acceptance and a low printing endurance.

[0010] EP-A- 003 789 discloses a process for the preparation of offset printing plates by means of an ink jet method with oleophilic inks. There is not indicated how said inks are made but from the examples it is clear that it concerns artificial latices, which are difficult to prepare.

55 [0011] JN- 57/038142 discloses a method of preparing a printing plate by forming an ink image on a blank printing plate, and also by fixing this image thermally by making toner adheres to this image-formed area. The composition of the ink is not mentioned, only the composition of the toners is disclosed.

[0012] JN- 07/108667 discloses a plate-making method forming an ink image containing a hydrophilic substance on a conductive support whose surface layer is made hydrophilic according to an electrostatic attraction type ink set sys-

tem to dry or cure the same, by applying bias voltage to the conductive support at the time of ink jet writing. This is a cumbersome process.

[0013] US-P- 5 213 041 discloses a method for preparing a re-usable printing plate for printing, projecting an imaging deposit on the plate surface by jet printing using an ejectable substance containing a heat fusible component. The image forms an imaging deposit which is fused to the surface of the printing plate using a variable frequency and variable power induction heater. This patent is silent about latices.

OBJECTS OF THE INVENTION

[0014] It is an object of the invention to provide a method for making lithographic printing plates from a lithographic base having a hydrophilic surface image-wise imaged with a hydrophobic polymer containing synthetic latex which yields an excellent lithographic printing plate with a good ink acceptance in the image areas and no ink acceptance in the non-image areas and a high printing endurance.

[0015] It is further an object of the present invention to provide a method for making lithographic printing plates without a wet development of the lithographic base in a rapid, economical and ecological way.

[0016] Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION

[0017] According to the present invention there is provided a method for making a lithographic printing plate comprising the steps of dispensing in a predetermined pattern a synthetic latex of particles of a hydrophobic polymer onto a hydrophilic surface of a lithographic base and heating said lithographic base to at least the glass transition temperature (T_g) of the hydrophobic polymer.

DETAILED DESCRIPTION OF THE INVENTION

[0018] According to the invention the lithographic base with a hydrophilic surface is heated after spraying said hydrophilic surface with droplets of the hydrophobic polymer synthetic latex in the predetermined pattern at a temperature preferably at least 5°C, more preferably at least 10°C higher than the T_g of said hydrophobic polymer.

[0019] In one embodiment said heating is carried out in an oven. In that case the lithographic base having a hydrophilic surface after being sprayed with droplets of the hydrophobic polymer synthetic latex in the predetermined pattern is heated preferably for at least one minute, more preferably for at least 5 minutes above the T_g of the hydrophobic polymer.

[0020] In another embodiment said heating is carried out by contacting to a hot body.

[0021] In another embodiment said heating is carried out with an IR-heater or laser. The time of heating is then the time of the laser dwell time, i.e. from 0.005 to 2 μs. This mode of heating requires that the lithographic base or the synthetic latex comprises a compound capable of converting laser-light to heat.

[0022] It is particularly preferred to use an infrared pigment or dye for that purpose. Particularly desirable in this invention is an infrared dye. However, pigments can be used as well such as e.g. carbon black, a conductive polymer particle, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. WO₂.9.

[0023] According to the present invention, the lithographic base may be an anodised aluminum support. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB-A- 1 084 070, DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760 and US-P- 4 458 005.

[0024] According to another mode in connection with the present invention, the lithographic base with a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-

linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetraalkylorthosilicate. The latter is particularly preferred.

[0025] As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylate acid, methacrylate acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

[0026] The amount of crosslinking agent, in particular of tetraalkyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, more preferably between 0.5 and 5 parts by weight, most preferably between 1.0 parts by weight and 3 parts by weight.

[0027] A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica may be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

[0028] The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 μm and is preferably 1 to 10 μm .

[0029] Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, US-P- 4 284 705 and EP-A- 514 490.

[0030] As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, substrated polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent. Also suitable as flexible support is glass with a thickness less than 1.2 mm and a failure stress (under tensile stress) equal or higher than 5×10^7 .

[0031] It is particularly preferred to use a polyester film support to which an adhesion improving layer has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A- 619 524, EP-A- 620 502 and EP-A- 619 525. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2 . Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

[0032] A latex is defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium. The polymer particles are usually approximately spherical and of typical colloidal dimensions: particle diameters range from about 20 to 1000 nm. The dispersion medium is usually a dilute aqueous solution containing substances such as electrolytes, surfactants, hydrophilic polymers and initiator residues. The polymer latices are classified in various way. By origin, they are classified as natural latices, produced by metabolic processes occurring in the cells of certain plant species; synthetic latices, produced by emulsion polymerization of monomers; and artificial latices, produced by dispersing a polymer in a dispersing medium.

[0033] A hydrophobic polymer for use in the present invention has preferably a T_g below 150°C , more preferably a T_g below 120°C . A hydrophobic polymer for use in the present invention has preferably a T_g of at least 30°C , more preferably a T_g of at least 35°C .

The hydrophobic polymer synthetic latex for use in the present invention may contain conventional emulsifiers.

[0034] Hydrophobic polymers for use in synthetic latices according to the present invention are, for example, polystyrene, polyacrylates such as polymethyl methacrylate and polybutyl acrylate, copolymers of butyl acrylate and methyl methacrylate, copolymers of butyl acrylate and styrene, homopolymers of butadiene, copolymers of butadiene and methyl methacrylate.

[0035] In order to facilitate the evaluation of the obtained lithographic plate colored hydrophobic polymer synthetic latices can be used. For example, carbon black or dyes or pigments can be mixed with one of the above mentioned homopolymers or copolymers. Also polymer particles containing color structures in the repeating units, in particular colored polymer particles which have obtained their color by means of a chemical reaction based on oxidative coupling of a color coupling group in the polymer structure of the particles with an aromatic primary amino compound, as described in Japanese Kokai 59/30873 can be used as colored hydrophobic polymer latex.

[0036] The hydrophobic polymer synthetic latex particles have preferably a particle size between 0.01 and 1 μm , more preferably between 0.01 μm and 0.25 μm .

[0037] The latex can contain from 1 to 60 % by weight of hydrophobic polymer, more preferably from 2 to 40 % by weight of hydrophobic polymer, most preferably from 5 to 20 % by weight of hydrophobic polymer.

[0038] The latex can be dispensed onto the lithographic base having a hydrophilic surface preferably by an ink jet printer.

5 **[0039]** A volatilization preventive agent is added to the latex according to the present invention, if necessary, to suppress evaporation of the liquid in the ink-jet nozzle and to prevent clogging due to precipitation of the dissolved or dispersed components.

[0040] A surfactant is preferably added to the latex used according to the present invention to adjust the size of droplets of the latex blowing out from the ink jet nozzle, to adjust the surface tension of the latex so that images can be
10 formed in high resolution.

[0041] Other components can be further added, if necessary, to the latex used according to the present invention. For example, heat polymerisation inhibitors, disinfectants, anticontamination agents and anti-fungal agents can be also added. Use of buffers and solubilizers is effective to improve the solubility or dispersibility of the polymer. Addition of defoaming agents and foam suppressing agents are also possible to suppress foaming of the latex in the ink-jet nozzle.

15 **[0042]** Optionally other components that enhance the latex quality can be added.

[0043] The image forming requires the following steps. On demand, microdots of the hydrophobic polymer latex are sprayed onto the lithographic base in a predetermined pattern as the plate passes through the printer or by a printhead shutteling over the plate. According to one embodiment of the invention, the microdots have a diameter of about 50µm. In the following step the lithographic base sprayed with hydrophobic polymer synthetic latex is heated to at least the Tg.
20 This can be done by irradiation, by convection or by contact with a hot surface e.g. in an oven, by flash exposure, by IR-heaters or by laser irradiation.

[0044] The image forming can also be carried out with the lithographic base already on the printing cylinder. In that case the heating of the polymer to a temperature at least equal to the Tg of said polymer can be effected by using a heated printing cylinder.

25 **[0045]** The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. This cylindrical printing plate has such a diameter that it can be slid on the print cylinder. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

[0046] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

30

EXAMPLE 1

Preparation of the synthetic latices.

35 **[0047]** Six synthetic latices were prepared all having 10% by weight of copolymer in water. Their composition and their Tg is given in table 1

table 1

40

Number	Monomer 1	%	Monomer 2	%	Tg
1	Butyl acrylate	13	Methyl methacrylate	87	82°C
2	Butyl acrylate	10	Methyl methacrylate	90	90°C
3	Butyl acrylate	35	Methyl methacrylate	65	52°C
4	Butyl acrylate	15	Styrene	85	50°C
5	Butyl acrylate	45	Styrene	55	34°C
6	Butadiene	50	Methyl methacrylate	50	28°C

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[0048] These latices were imagewise jetted on an hydrophilic support, said support being anodized aluminum or a layer of hardened polyvinyl alcohol on polyethylene terephthalate. These supports were prepared as follows:

55 Preparation of the anodized aluminum support

[0049] 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/m² to form a surface topography with an average center-line roughness Ra of 0.5 µm.

[0050] 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.

[0051] 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/m² for about 300 seconds to form an anodic oxidation film of 3.00 g/m² of Al₂O₃ 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 a layer of hardened polyvinyl alcohol on polyethylene terephthalate

Preparation of the solution for the subbing layer.

[0052] To a solution of 11.4 g of gelatine (viscosity : 19-21 mPas) in 940 ml of water was added 31.7 ml (11.4 g solid product) KIESELSOL 300 F (tradename for 30 % aqueous dispersion of colloidal silica - surface area of 300 m² per g). Anionic wetting agents (0.6 g) and biocides (1 g) were added.

Preparation of the hydrophilic layer.

[0053] To 440 g of a dispersion containing 21.5 % TiO₂ (average particle size 0.3 to 0.5 µm) and 2.5 % polyvinyl alcohol in deionized water were subsequently added, while stirring, 250 g of a 5 % polyvinyl alcohol solution in water, 105 g of a hydrolyzed 22 % tetramethyl orthosilicate emulsion in water and 22 g of a 10 % solution of a wetting agent. To this mixture was then added 183g of deionized water and the pH was adjusted to pH=4.

Preparation of the hydrophilic support

[0054] To a polyethylene terephthalate support, coated with a primer containing 170 mg/m² of a latex of copoly(vinylidenechloride/ methyl methacrylate/ icatonic acid) and 40 mg/m² of silica with a surface area of 100 m²/g was applied the above described solution for the subbing layer at a solids coverage of 750 mg/m². On top of the subbing layer was coated the above mentioned hydrophilic layer to a wet coating thickness of 50 g/m², dried at 30°C and subsequently hardened by subjecting it to a temperature of 60°C for 1 week.

[0055] On one of those supports two samples were imaged with latex composition 1-6, one was left as such for 30 minutes and then applied on a AB-Dick 360 printing press and printed with conventional ink (Van Son rubberbase) and a commercial fountain (2% Tame) The other sample was heated in an oven for 25 minutes and then cooled during 5 minutes to room temperature before being used as printing plate. The printing results are given in table 2.

Table 2

Support	Latex	Heating temperature	Ink accept.	Endurance
PTT	1	25°C	-	-
PTT	1	100°C	++	+
PTT	2	25°C	-	-
PTT	2	100°C	++	+
PTT	3	25°C	-	-
PTT	3	100°C	++	-
PTT	4	25°C	-	-
PTT	4	100°C	+	++
PTT	5	25°C	-	-
PTT	5	40°C	+	-
ALU	6	25°C	-	-

Table 2 (continued)

Support	Latex	Heating temperature	Ink accept.	Endurance
ALU	6	40°C	++	+

-Support: Alu (anodized aluminum) or PTT (polyvinyl alcohol hardened layer)
 -Ink acceptance:
 -- none
 - very low density
 + correct after 10 copies
 ++ correct after 1 to 5 copies
 -Endurance
 -- printing image practically immediately disappeared
 - printing image obtains only 100 copies
 + only slight wear on the printing image after 100 copies
 ++ no wear on the printing image after 100 copies.

[0056] It is seen that all the samples which were not heated above their Tg showed a poor result as well for their ink acceptance as for their endurance. All the samples which were heated above their Tg showed at least a good result for their ink acceptance and in most cases also a good result for their endurance.

Claims

1. A method for making a lithographic printing plate comprising the steps of dispensing in a predetermined pattern a synthetic latex of particles of a hydrophobic polymer onto a hydrophilic surface of a lithographic base and heating said lithographic base to at least the glass transition temperature (Tg) of the hydrophobic polymer.
2. A method according to claim 1 wherein said heating is to a temperature at least 5°C above the Tg of the hydrophobic polymer.
3. A method according to claim 1 or 2 wherein said hydrophobic polymer synthetic latex contains from 1 to 60 % by weight of hydrophobic polymer.
4. A method according to any of claims 1 to 3 wherein said hydrophobic polymer synthetic latex particles have a particle size from 0.01 μm to 1 μm .
5. A method according to any of claims 1 to 4 wherein the hydrophobic polymer has a Tg below 150°C.
6. A method according to any of claims 1 to 5 wherein the lithographic base having a hydrophilic surface is an anodized aluminum support or a flexible support provided with a cross-linked hydrophilic layer.
7. A method according to any of claims 1 to 6 wherein said synthetic latex contains a dye or a pigment
8. A method according to any of claims 1 to 7 wherein a synthetic latex comprises a monomer selected from the group consisting of styrene, butyl acrylate, methyl methacrylate and butadiene.
9. A method according to any of claims 1 to 8 wherein said heating occurs by irradiation, convection or contact with a heated surface.
10. A method according to any of claims 1 to 9 comprising the steps of mounting a lithographic base having a hydrophilic surface on a print cylinder of a printing press, dispensing in a predetermined pattern a synthetic latex of particles of a hydrophobic polymer onto said hydrophilic surface and heating said lithographic base to at least the glass transition temperature (Tg) of the hydrophobic polymer.



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EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1313

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 September 1999	Examiner Philosoph, L
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EUROPEAN SEARCH REPORT

Application Number
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<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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

EP 99 20 1313

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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