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(54) Method for making lithographic printing plates using a novolac resin

(57) According to the present invention there is provided a method for making a lithographic printing plate

comprising the step of dispensing in a predetermined pattern a novolac resin onto a hydrophilic surface of a lithographic base.

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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 novolac resins, which makes it possible to produce the lithographic plates directly from digital data output from computers, facsimiles, or the like without using any intermediate films having negative or positive images.

10 BACKGROUND OF THE INVENTION.

15 **[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 an intermediate film for making printing plates.

20 **[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.

25 **[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.

50 **[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.

55 **[0010]** **EP-A- 776 763** discloses a method for producing a lithographic printing plate containing a printable resinous image comprising: depositing a liquid comprising at least one reactant of a resin producing reaction mixture onto said plate employing at least one printer head in a predetermined image-reproducing manner, said liquid deposited onto said plate in contact with remaining reactants necessary to complete said mixture on the surface of said plate; and polymerizing said complete mixture on said plate under resin polymerization conditions whereby said lithographic plate containing a printable resinous image is produced. This is a cumbersome manner for producing a printing plate by ink jet.

OBJECTS OF THE INVENTION

[0011] 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 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.

[0012] 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.

[0013] Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION

[0014] According to the present invention there is provided a method for making a lithographic printing plate comprising the step of dispensing in a predetermined pattern a novolac resin onto a hydrophilic surface of a lithographic base.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A novolac is any of the phenol-formaldehyde resins made with an excess of phenol in the reaction. Said phenol can be phenol, cresol etc. Preferred novolac resins are poly (cresol-xylanol-formaldehyde) resins and poly (phenol-xylanol-formaldehyde) resins. The novolac resin is dispersed in an aqueous medium or dissolved in an organic solvent. Suitable organic solvents are e.g. 1-methoxy-2-propanol, ethyl acetate, methyl ethylketone and isopropanol. The concentration of the resin in solution ranges from 5 to 50 % by weight, more preferably from 10 to 30 % by weight. The concentration of novolac resins in an aqueous dispersion ranges from 5 % to 80 % by weight, more preferably from 20 to 60 % by weight. The novolac resins according to the invention have a molecular weight of at least 1000, more preferably of at least 5000, most preferably of at least 10000. Said novolacs could comprise an epoxy group.

[0016] The novolac resin is a hydrophobic, oleophilic resin. In the present invention, a hydrophobic oleophilic compound is a compound that, when brought in a mixture of water and oil, is wetted by oil while a hydrophilic compound, when brought in a mixture of water and oil, is wetted with water.

[0017] According to the invention the lithographic base with a hydrophilic surface is preferably heated after spraying said hydrophilic surface with droplets of the hydrophobic polymer in the predetermined pattern at a temperature of preferably at least 45°C, more preferably at least 55°C.

[0018] 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 in the predetermined pattern is heated preferably for at least one minute, more preferably for at least 5 minutes.

[0019] In another embodiment said heating is carried out by contacting to a hot body.

[0020] 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 us. This mode of heating requires that the lithographic base or the novolac resin solution or dispersion comprises a compound capable of converting laser-light to heat.

[0021] 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.

[0022] In order to improve the abrasion resistance, there can be added curing agents to the solution or more preferably to the dispersion of said novolac resin. Suitable curing agents are amines such as Jeffamine™, trade name of Texaco Chemical Co and Euredur TB03345™, trade name of Witco Chemical Cob but also mercaptans or alcohol groups containing components can be used. Said curing agents are preferably used in an amount of 5 to 80 % by weight of the novolac.

[0023] According to the invention, coupling agents can be added to the solution or dispersion of a novolac in order to improve the adhesion between said novolac and the hydrophilic surface of the lithographic support. Suitable coupling agents are alkoxy silanes with a amino- or an epoxy function, but other adhesion improving functions are also possible. Said coupling agents are preferably used in an amount of 2 to 10 % by weight.

[0024] 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, DB-A- 4 001 466, EP-A- 292 801, EP-A- 291 760** and **US-P- 4 458 005**.

[0025] 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.

[0026] 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/vinylmethylene 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.

[0027] 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.

[0028] 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.

[0029] 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.

[0030] 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**.

[0031] 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 .

[0032] 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 m² and 750 mg per m². 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 m² per gram, more preferably at least 500 m² per gram.

[0033] The novolac dispersion is defined as a stable colloidal dispersion of a novolac substance in an aqueous medium. The novolac 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

[0034] In order to facilitate the evaluation of the obtained lithographic plate colored hydrophobic novolac resins can be used. For example, carbon black or dyes or pigments can be mixed with a novolac resin.

[0035] The novolac resin can be dispensed onto the lithographic base having a hydrophilic surface preferably by an ink jet printer.

[0036] A volatilization preventive agent is added to the ink 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.

[0037] A surfactant is preferably added to the ink according to the present invention to adjust the size of droplets

of the dispersion blowing out from the ink jet nozzle, to adjust the surface tension of the ink so that images can be formed in high resolution.

[0038] Other components can be further added, if necessary, to the ink 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 ink in the ink-jet nozzle.

[0039] Optionally other components that enhance the dispersion quality can be added.

[0040] The image forming requires the following steps. On demand, microdots of the hydrophobic novolac resin 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 30 μ m. In the following step the lithographic base sprayed with hydrophobic novolac resin can be heated. 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.

[0041] The image forming can also be carried out with the lithographic base already on the printing cylinder. In that case the optional heating of the novolac resin can be effected by using a heated printing cylinder.

[0042] 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.

[0043] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Preparation of the novolac solutions.

[0044] Seven solutions were prepared:

- Solution 1: 15 % of a modified high molecular weight phenolic resin in methyl ethyl ketone.(Albertol KP 648 TM- Chemische werke Albert).
- Solution 2: 10 % of a modified high molecular weight phenolic resin in ethyl acetate.(idem)
- Solution 3: 10 % of a modified phenolic resin in methyl ethyl ketone.(Krumphaar K4733 TM-Lawter international)
- Solution 4: 10 % of a phenolic resin in methyl ethyl ketone.(Durez 28391 TM-Occidental Chemical)
- Solution 5: 6 % solution of Alnovol TM in isopropanol. Alnovol is a trade name for a cresol formaldehyde resin from Clariant, Germany.
- Solution 6: 14 % solution of Alnovol TM in isopropanol.
- Solution 7: 10 % solution of Alnovol TM in isopropanol. In this examples the solution is sprayed on a hardened polyvinyl alcohol on a P.E.T. plate with a HP690C. From each of these plates, 2500 copies were printed.

Preparation of a layer of hardened polyvinyl alcohol on polyethylene terephthalate

Preparation of the solution for the subbing layer.

[0045] 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.

[0046] To 440 g of a dispersion containing 21.5 % TiO₂ (average particle size 0.3 to 0.5 μ m) 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

[0047] 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.

[0048] The results are given in table 1.

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table 1

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Solution	Abrasion	Ink Acceptance
1	++	+++
2	+	++
3	++	++
4	++	+++
5	++(+)	+++
6	+++	+++
7	+++	+++

-Ink acceptance:

- none
- very low density
- + correct after 10 copies
- ++ correct after 3 to 5 copies
- +++ correct after 1 copy

-Abrasion

- apparent wear after 2500 copies
- + slight wear after 2500 copies
- ++ very slight wear after 2500 copies
- +++ no wear after 2500 copies.

[0049] As seen, all solutions gave a good to a very good printing result.

EXAMPLE 2

[0050] Two dispersions of a novolac resin were prepared:

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- Dispersion 1: 100 g of Epi-Rez 5003-W-55 TM, trade name of Shell Co for a bisphenol-A novolac and 17.8 g of Euredur TB 03J544 TM, an amine curing agent from Witco Chemical Co per 100 ml of water.
- Dispersion 2: 100 g of Epi-Rez 5003-W-55 TM, trade name of Shell Co for a bisphenol-A novolac and 88.8 g of Euredur TM, an amine curing agent from Witco Chemical Co per 100 ml of water.

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These dispersions were imagewise jetted on an hydrophilic support, said support being anodized aluminum or a layer of hardened polyvinyl alcohol on polyethylene terephthalate. The anodized aluminum was prepared as follows:

Preparation of the anodized aluminum support

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[0051] 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 μ m.

[0052] 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.

[0053] 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.

On each of those supports two samples were imaged with dispersion composition 1-2, 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 at 60°C 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.

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Table 2

Dispersion	Support	Drying	Ink Acceptance	Abrasion
1	PTT	-	++	+/-
1	PTT	60°C	++	+
1	ALU	-	++	++
1	ALU	60°C	++	++
2	PTT	-	+++	+/-
2	PTT	60°C	++	++
2	ALU	-	++	++
2	ALU	60°C	++	++

20 [0054] Ink acceptance and abrasion are defined as set out in example 1

- Support:Alu (anodized aluminum) or PTT (polyvinyl alcohol hardened layer)

25 [0055] It is seen that all the samples gave a good ink acceptance and that the samples coated on aluminium or PTT after heating gave an acceptable to a good abrasion.

Claims

- 30 1. A method for making a lithographic printing plate comprising the step of dispensing in a predetermined pattern a novolac resin onto a hydrophilic surface of a lithographic base.
2. A method for making a lithographic printing plate according to claim 1 wherein said novolac resin is a poly-[cresol-xylenolformaldehyde] resin or a poly-[phenol-xylenol-formaldehyde] resin.
- 35 3. A method according to claim 1 or 2 wherein said novolac is dissolved in an organic solvent.
4. A method according to claim 3 wherein the concentration of the resin in solution ranges from 5 to 50 % by weight.
5. A method according to claim 1 or 2 wherein said novolac is dispersed in an aqueous medium.
- 40 6. A method according to claim 5 wherein the concentration of the resin in dispersion ranges from 5 to 80 % by weight.
7. A method according to any of claims 1 to 6 wherein said novolac comprises a curing agent.
- 45 8. A method according to any of claims 1 to 7 wherein said novolac comprises a coupling agent.
9. A method according to any of claims 1 to 8 wherein said dispensing step is carried out by an ink jet apparatus.

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EUROPEAN SEARCH REPORT

Application Number
EP 99 20 1217

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search		Examiner
THE HAGUE	3 September 1999		Bacon, A
CATEGORY OF CITED DOCUMENTS			
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			
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			

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

EP 99 20 1217

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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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