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(54) **Lithographic printing plate for laser direct plate making requiring no liquid developing treatment process and printing method using the same**

(57) Disclosed is a lithographic printing plate for a laser direct plate making requiring no liquid developing treatment process, in which a pulsed ultraviolet laser having a wave length in an ultraviolet range is image-wise irradiated on a thermoplastic polymer film having the absorption band range in an ultraviolet range to impart hydrophilicity to the irradiated portion of the thermoplastic polymer, and a method for offset printing using the same.

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Description

FIELD OF THE INVENTION

The present invention relates to a lithographic printing plate requiring no liquid developing treatment process (hereinafter abbreviated as developing process) in which a thermoplastic polymer film having a high glass transition temperature and a strong absorption band in an ultraviolet range is exposed to a pulsed ultraviolet laser having an absorption band range in the ultraviolet range to impart hydrophilicity to the irradiated portion of the polymer. The lithographic printing plate of the present invention is especially used in an offset printing utilizing repulsion between water and oil.

BACKGROUND OF THE INVENTION

A printing plate is roughly classified from the viewpoint of printing manner into a letter press printing plate, a lithographic printing plate used in an offset printing, an intaglio printing plate used in a gravure printing, or a screen printing plate. These printing manners are selected according to kind of an object to be printed, printing quality, the number of printing copies, or managing policy and nature of a printing company. Among them, offset printing has enlarged and diversified its market in the fields of general commercial printing paper printing package material printing and the like because of rapid developments in a photosensitive material technique and a system technique of a photographic plate making, and has occupied more than 80 % of whole printing industry.

In the offset printing, a printing plate comprising an aluminum base and a photosensitive material coated on the aluminum base (referred as PS plate) has been mainly used. PS plate is exposed to an active beam discharged from a mercury electric discharge lamp or laser through a plate making photographic film having an image information, and then developed by removing a photosensitive substance on an exposed or unexposed portion with a developing liquid (referred as development) to form a printing plate. The offset printing using PS plate does not meet the demands of the plate making industry, for example lowering of a plate making cost, shortening of a plate making time, reduction of the treatment of waste developing liquid and the like.

With such enlargement and diversification of the offset printing market, various new printing systems and lithographic printing plate materials suitable for the systems were proposed. Their examples are as follows: (1) a computer-to-plate system in which a plate or image carrier is made without using a photographic film for plate making, and printing is conducted on an object to be printed, (2) a computer-to-print system such as electrophotography, magnetography, ionography or ink jet in which printing is directly conducted on an object to be printed without using a photographic film for plate making or a plate. In these two systems, the method (1) is

used in a large number printing field, and the method (2) is used in a relatively small number printing, printing by word processor or on-demand printing. They are developing corresponding to a diversifying offset printing.

The printing industry is gradually moving to printing of many kinds of articles with small number and to color printing. It has been therefore desired to develop a system corresponding to the movement. One good system is the above mentioned computer-to-plate system (1).

The printing plate used for the computer-to-plate system (1) has to have a photosensitive layer having photosensitivity enough to form an image by a low output laser, and does not require wet developing treatment which uses liquid developer.

However, a technique now on developing is a multi layer structure or uses a specific material and plate making apparatus. For example, an electric discharge destruction type print plate is obtained by making a picture forming layer consisting of an aluminum metal layer and a silicone layer on a PET film, and both layers are destructed by a multistylus electric discharge head modulated by an image signal to form an ink receiving layer, thus forming a printing plate.

If a printing plate suitable for the computer-to-plate system is obtained by using a generally used polymer material and an existing apparatus without using such specific material and plate making apparatus, a great contribution to the printing industry may be expected.

PROCESS TO REACH THE PRESENT INVENTION

The present inventors proposed in JOURNAL OF PHOTOPOLYMER SCIENCE AND TECHNOLOGY, the 4th edition, No.3 (1991), pp 463 - 468 and the 7th edition, No.2 (1994), pp 299 - 308 that a thermoplastic resin film was irradiated by laser to divide into a hydrophilic area and a hydrophobic area.

The present inventors, however, thought that the methods disclosed in the above two literatures was very interesting but it was difficult to apply the methods to lithographic printing. It was because, even if hydrophilicity might be obtained by a laser irradiation, a large number printing was impossible by lithographic printing unless the thermoplastic resin film had a water retention as well as hydrophilicity. In the aforementioned literatures, it is disclosed that a depth of corrosion obtained by a laser irradiation is approximately 1 μm , and therefore, an enough water retention may not be expected to exist. Further, although a depth of corrosion may be made deeper by conducting abrasion more to improve water retention, several J/cm^2 of energy is required in such case and simplicity of the direct printing is lost.

In spite of the aforementioned fear of the present inventors, an actual application of the method to printing unexpectedly showed high printing performance and the printing plate also had high water retention and hydrophilicity. This was surprising to the inventors. The reason is now under consideration and is not certain,

but it is presumed that its polymer surface is to be porous.

OBJECTS OF THE INVENTION

The object of the present invention is to provide a lithographic printing plate for laser direct plate making requiring no liquid developing treatment process, by irradiating a pulsed ultraviolet laser having a specific wave length on a commercially available polymer material.

Further objects, advantages and features will become more apparent with the teaching of the principles of the invention in connection with the disclosure of the preferred embodiments in the specification, claims.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a lithographic printing plate for laser direct plate making requiring no liquid developing treatment process, in which a pulsed ultraviolet laser having a wave length in an ultraviolet range is imagewise irradiated on a thermoplastic polymer film having the absorption band range in an ultraviolet range to impart hydrophilicity to the irradiated portion of the thermoplastic polymer.

The present invention also provides a method for offset printing, in which a pulsed ultraviolet laser having a wave length in an ultraviolet range is imagewise irradiated on a thermoplastic polymer film having an absorption band range in an ultraviolet range to form an image and then an ink for lithographic printing is applied on the thermoplastic polymer film to conduct printing.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, a laser drawing is directly conducted on a generally used thermoplastic polymer film having a high glass transition temperature (hereinafter abbreviated as T_g) and a high ultraviolet absorbance, thus providing technical effects such as lowering of cost of a printing plate and print making, making clean of a print making environment, dispelling of uneasiness of material supply and the like. That is, a thermoplastic polymer having a high T_g and having art absorption band in an ultraviolet range is irradiated by an ultraviolet pulse laser having an energy just in the absorption band range, to enhance hydrophilicity of an irradiated surface and to realize a selective sticking of an ink.

The thermoplastic polymer film having an absorption band in an ultraviolet range may have T_g of not less than 160°C and an absorbance in a wave length of a laser of not less than $1 \times 10^2 \text{ cm}^{-1}$. Concretely, it includes a polyimide resin, polyphenylquinoxaline (PPQ) and polysulfone, or a polymer having these polymer structures. In the polyimide resin, especially a film obtained by polycondensation, for example, Kapton film available from Du Pont company (USA) is more suitable.

Film thickness is optionally controlled, however, a thickness of not less than 50 μm is preferred in order to satisfy mechanical strength and physical conditions required as a printing plate. As described above, the film can be a printing plate as a single substance, however, a thermoplastic film layer may be optionally formed on a support substance (for example, various dimension stable plastic sheets, papers, metal plates as a single substance or their laminate).

The thermoplastic polymer film may also be formed by applying an organic solvent solution of the polymers on the support substance and then by removing the solvent. Or the thermoplastic polymer film may also be formed by applying a precursor solution of the polymers on the support substance and then conducting thermosetting. 1) The organic solvent solution includes a solution of a polyimide resin having an aromatic ring soluble in an organic solvent (MATRIMID 5218: commercial name, manufactured by CIBA-GEIGY company) dissolved in a specific organic solvent, and the like. 2) The precursor solution includes a fluorohydrocarbon solution of a polyamide resin having an aromatic ring soluble in an organic solvent (for example, a resin obtained by a solution polymerization in a solvent of 3,3',4'-benzophenone tetracarboxylic anhydride with 3,3'-diaminobenzophenone), or of a copolymer of tetrafluoroethylene with 2,2'-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxolene (TEFLON AF: commercial name), and the like. An applied film of the aforementioned polymer is made into a thermoplastic polymer film by a heat treatment.

The laser as light source is a pulse type UV laser, and a multi mode Nd: YAG laser (4th harmonic mode: 266 nm, and 3rd harmonic mode: 355 nm), ArF excimer laser (wavelength: 193 nm), KrF excimer laser (wavelength: 248 nm) or XeCl excimer laser (wavelength: 308 nm). From the viewpoint of easiness of maintenance, YAG laser is more preferable than excimer laser. An energy density (fluence) required for enhancing hydrophilicity is in a range of 10 - 100 mJ/cm^2 . if over 100 mJ/cm^2 , printing suitability is not improved, although abrasion becomes extreme and surface roughness increases. There is a threshold value of an energy density to impart hydrophilicity to a surface to be irradiated. Therefore, a pulse is necessary which has a big peak output due to a short strong pulse electric discharge. Hydrophilicity can not be enhanced by irradiation of sequential excitation type laser or mercury lamp beam. To effectively absorb an energy, the film should have a light absorbance of not less than $1 \sim 10^2 \text{ cm}^{-1}$, preferably $5 \times 10^2 - 5 \times 10^3 \text{ cm}^{-1}$.

The laser irradiation can enhance hydrophilicity when the irradiation is carried out in any of the air, water and an alkaline solution such as tetramethyl ammonium hydroxide. Hydrophilicity may be expressed by a change of a contact angle against water. When laser irradiation of 40 mJ/cm^2 is conducted, a contact angle against water varies from 80° to 0°. in the printing industry, it is proposed that an offset printing is possible if a

contact angle against water on a printing plate is not more than 20°. Any printing plates of the present invention suffice this value.

Hydrophilicity increases in the order of polyester < polysulfone < Kapton $\approx$ PPQ. Polycarbonate, polystyrene, and polymethylmethacrylate show little hydrophilicity. Hydrophilicity of these polymers decreases as T_g decreases. It is considered that by laser irradiation, abrasion occurs, and irradiated part become porous, plus charge is generated on the surface and surface roughness increases to give hydrophilicity. It is presumed that when T_g is high, the surface roughness and the porous structure of a surface part made by the irradiation may be maintained. For manifestation and maintenance for long period of hydrophilicity, T_g of the polymer should be at least not less than 160 °C. Although hydrophilicity of the irradiated part may be maintained for at least several months, for obtaining a practical printing plate, hydrophilicity should be maintained semipermanently. For such semipermanent maintenance, a conventional desensitizing method which uses phosphoric acid as a main component may be adopted.

Picture formation is conducted by scanning and irradiating a laser previously modulated with a image signal. As an apparatus for scanning and irradiating, an apparatus developed for the other computer-to-plate system can be used only if a laser light source is changed.

In another method for image formation, a mask having a image information is laid on the aforementioned thermoplastic polymer film, and the aforementioned laser is irradiated thereon. As the mask, a photographic negative film, a metal mask and the like can be used.

In the printing industry, as a part of structural improvement of the industry, simplification of a plate making process and lowering of cost are desired. The present invention has been contrived to suffice these requirement. By the present invention, a printing plate can be manufactured only by using a generally used polymer film and by irradiating a laser beam on the surface, and a printing plate is provided which requires no developing treatment process. Therefore, the present invention is useful for development of the printing industry.

EXAMPLES

The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

Example 1

Kapton film (manufactured by Du Pont company; film thickness is 50 μ m) was scanned and exposed to Nd: YAG laser (4th synchronized mode: 266 nm, manufactured by Spectra Physics company, Quanta-Ray

GCR-4) at an energy density of 14 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 2

Kapton film (manufactured by Du Pont company; film thickness is 50 μ m) was scanned and exposed to ArF excimer laser (wave length: 193 nm, manufactured by Lambda Physik company) at an energy density of 20 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 3

PPQ film (commercially available from CEMOTA company; polyphenylquinoxaline) instead of Kapton film was scanned and exposed to Nd: YAG laser (4th harmonic mode: 266 nm) at an energy density of 14 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 4

PPQ film (commercially available from CEMOTA company; polyphenylquinoxaline) instead of Kapton film was scanned and exposed to ArF excimer laser (wave length: 193 nm) at an energy density of 20 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 5

An etching liquid for light offset printing (Ricoh Fax Etch Liquid) was applied on the film of Example 1, and a desensitizing treatment was conducted to find no change in a contact angle after half a year.

The aforementioned etching liquid was diluted with water to prepare a wetting water, and printing was conducted. A process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) and a fine quality printing paper were used. A printed article having an excellent image reproductivity equivalent to a conventional PS plate was obtained.

Example 6

A mask having a image information was closely laid on Kapton film (manufactured by Du Pont company; film thickness is 50 μm), and thus obtained complex was exposed to Nd: YAG laser (3th harmonic mode: 355 nm, manufactured by Spectra Physics company, Quanta-Ray GCR-4) at an energy density of 14 mJ/cm² and a pulse width of 15 nsec.

An etching liquid for light offset printing (Ricoh Fax Etch Liquid) was diluted with water to prepare a wetting water, and printing was conducted. A process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) and a fine quality printing paper were used. An excellent printed article which reproduces a image of the mask was obtained.

Example 7

An diethyleneglycoldimethylether solution of polyamide acid having a solid content of 30% (viscosity at 25°C: 20,000 cps) (obtained by a solution polymerization in a solvent of 3,3',4'-benzophenonetetracarboxylic anhydride with 3,3'-diaminobenzophenone) was applied (wet film thickness: 7 μm) on an aluminum plate by a spin coater. Thermosetting was conducted at 300°C for 30 minutes.

Thus obtained coating plate was scanned and exposed to Nd: YAG laser (4th harmonic mode: 266 nm, manufactured by Spectra Physics company, Quanta-Ray GCR-4) at an energy density of 14 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 8

An N-methylpyrrolidone solution of a soluble polyimide (commercial name: MATRIMIDE 5218, manufactured by CIBA-GEIGY company) (solid content: 20%) was applied on an aluminum plate by a spin coater. Drying was conducted to remove the solvent.

Thus obtained coating plate was scanned and exposed to Nd: YGA laser (4th harmonic mode: 266 nm, manufactured by Spectra Physics company, Quanta-Ray GCR-4) at an energy density of 14 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 9

The film of Example 1 was scanned and exposed to ArF excimer laser (wave length: 193 nm) at an energy density of 20 mJ/cm² and a pulse width of 15 nsec.

Water was dropped on a sample and a contact angle was measured using a goniometer type contact angle measuring apparatus to find an angle of approximately 0°, when irradiation was conducted in the air.

A solution prepared by diluting an etching liquid for light offset printing (Ricoh Fax Etch Liquid) with water was used as a wetting water. An ink sticking characteristic to the surface of the film was examined using a process ink (CAPS-G: manufactured by Dainippon Ink & Chemicals, Inc.) to find that the irradiated part repelled the ink and the ink stuck to the unirradiated part.

Example 10

A copolymer of tetrafluoroethylene with 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxolene soluble in an organic solvent was dissolved in fluorohydrocarbon, and the resulting solution was spin-coated on an alumi-

num plate. Drying with heating was conducted to evaporate the solvent. A wet film thickness was previously controlled so as to obtain a dry film thickness of 10 μm . The coating film was doped by 25% by weight of tri- C_9F_{18} substituted triazine, then was heated at 200°C for 1 hour and irradiated by an ultraviolet beam to find an improved ultraviolet absorption (absorbance: 0.14, wave length: 240 nm). Thus obtained plate having the coating film was treated in the same manner as Example 1 to obtain a lithographic printing plate.

Claims

1. A lithographic printing plate for laser direct plate making requiring no liquid developing treatment process, in which a pulsed ultraviolet laser having wave length in an ultraviolet range is imagewise irradiated on a thermoplastic polymer film having the absorption band range in an ultraviolet range to impart hydrophilicity to the irradiated portion of the thermoplastic polymer.
2. A lithographic printing plate according to claim 1, wherein the pulsed ultraviolet laser is previously modulated by a image signal and, scanned and irradiated.
3. A lithographic printing plate according to claim 1, wherein the pulsed ultraviolet laser is irradiated through a mask having a image information.
4. A lithographic printing plate according to claim 1, wherein the thermoplastic polymer has a glass transition temperature of not less than 160°C and has an absorbance in the oscillation wave length of the laser of not less than $1 \times 10^2 \text{ cm}^{-1}$.
5. A lithographic printing plate according to claim 4, wherein the thermoplastic polymer is at least one selected from the group consisting of a condensation type polyimide resin, polyphenylquinoxaline and polysulfone, or is a polymer having in a polymer structure selected from the group of a condensation type polyimide resin, polyphenylquinoxaline and polysulfone.
6. A lithographic printing plate according to claim 1, wherein the pulsed ultraviolet laser is a pulse oscillation type Nd: YAG laser (wave length; 266 nm, 355 nm), ArF excimer laser (wave length; 193 nm), KrF excimer laser (wave length; 248 nm) or XeCl excimer laser (wave length; 308 nm).
7. A lithographic printing plate according to claim 1, wherein the thermoplastic polymer film is stuck on a dimension stable plastic sheet, paper or metal plate to make a two ply structure.
8. A lithographic printing plate according to claim 7, wherein the thermoplastic polymer film is stuck on the dimension stable plastic sheet, paper or metal plate using an adhesive to make a two ply structure.
9. A lithographic printing plate according to claim 1 or claim 7, wherein the irradiation part is desensitized.
10. A lithographic printing plate according to claim 1 or claim 7, wherein the thermoplastic polymer film is formed by applying a solution comprising the thermoplastic polymer and a solvent on a supporting substrate made of a plastic sheet, paper or metal plate and then removing the solvent.
11. A lithographic printing plate according to claim 1, wherein the thermoplastic polymer film is formed by applying a solution comprising a precursor of the thermoplastic polymer on a supporting substrate made of a plastic sheet, paper or metal plate and then conducting a heat treatment.
12. A lithographic printing plate according to claim 11, wherein the precursor is a polyamide resin having an aromatic ring, which is soluble in an organic solvent and is made into a polyimide resin by thermosetting.
13. A lithographic printing plate according to claim 11, wherein the precursor is a fluorohydrocarbon solution of a copolymer of tetrafluoroethylene with 2,2-bis (trifluoromethyl)-4,5-difluoro-1,3-dioxolene, and the thermoplastic polymer film is formed by doping the solution by perfluoroalkyl-substituted triazine and irradiating an ultraviolet light.
14. A method for offset printing, in which a pulsed ultraviolet laser having a wave length in an ultraviolet range is imagewise irradiated on a thermoplastic polymer film having an absorption band range in an ultraviolet range to form an image and then an ink for lithographic printing is applied on the thermoplastic polymer film to conduct printing.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 10 7779

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.6)
X	DD-A-103 977 (TRAUZEDDEL ET AL.) * the whole document *	1-14	B41C1/10
X	GB-A-1 511 626 (HOECHST AG)	1	
Y	* the whole document *	1-14	
Y	MICROELECTRONIC ENGINEERING, vol. 13, no. 1 / 04, 1 March 1991, pages 429-432, XP000220011 HIROYUKI HIRAOKA: "LASER PHOTOETCHING OF DOPED POLY(TETRAFLUOROETHYLENE), SUBSTITUTED -PFTE, AND POLYIMIDE FILMS" * the whole document *	1-14	
A	NL-C-108 794 (J. SCHERPENHIJSEN) * the whole document *	1	
Y	US-A-4 786 358 (YAMAZAKI SHUNPEI ET AL) 22 November 1988 * the whole document *	3	
A	US-A-4 036 136 (TAKAGI TOHRU) 19 July 1977	1-14	
Y	* column 2, line 6; claims; example 3 *	7,8,10, 11	B41C G03F
Y	* column 3, line 3 - line 41 *		
Y	* column 4, line 12 *		
Y	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. AN-4204150, May 1991 LAZARE ET AL.: "UV-laser photoablation of thermostable polymers : polyimides polyquinoxaline and Teflon AF" XP002010640 * abstract * & SYMPOSIUM , ANAHEIM , CA, USA 05.91, -----	4,5, 12-14	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 August 1996	Examiner Rasschaert, 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			

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