



**(12)**

**EUROPEAN PATENT APPLICATION**

**(21) Application number : 92305857.2**

**(51) Int. Cl.<sup>5</sup> : G03G 13/28**

**(22) Date of filing : 25.06.92**

**(30) Priority : 26.06.91 JP 182970/91**

**(43) Date of publication of application :  
30.12.92 Bulletin 92/53**

**(84) Designated Contracting States :  
DE GB**

**(71) Applicant : KONICA CORPORATION  
26-2, Nishi-shinjuku 1-chome Shinjuku-ku  
Tokyo (JP)**

**(72) Inventor : Hirai, Katsura, Konica Corporation  
1, Sakura-machi  
Hino-shi, Tokyo (JP)  
Inventor : Goto, Kiyoshi, Konica Corporation  
1, Sakura-machi  
Hino-shi, Tokyo (JP)  
Inventor : Kojima, Yasuo, Konica Corporation  
1, Sakura-machi  
Hino-shi, Tokyo (JP)**

**(74) Representative : Ellis-Jones, Patrick George  
Armine  
J.A. KEMP & CO. 14 South Square Gray's Inn  
London WC1R 5LX (GB)**

**(54) Method for manufacturing planographic printing plates.**

**(57)** A method of preparing a planographic printing plate from a light-sensitive planographic printing plate comprising an electrically conductive support provided thereon with a photoconductive layer comprising a photoconductor and an alkali soluble resin, said layer having a thickness of from 0.5 to 30  $\mu\text{m}$ , said method comprising :  
charging the photoconductive layer ;  
forming an electrophotographic latent image on the charged layer imagewise from an original image ;  
developing the latent image by applying toner to the exposed layer to form a toner image ; and  
removing with an alkali solution that part of the photoconductive layer on which the toner image is not formed to form a relief image on the support ;  
wherein the toner image is larger than the original image.

## FIELD OF THE INVENTION

The present invention relates to a method for manufacturing planographic printing plates. More particularly, the present invention relates to a method for manufacturing planographic printing plates free from the problem caused by side etching in the etching process, which arises in plate making comprising the steps of forming toner images, through the electrophotographic process, on a planographic printing plate comprising a conductive support and a photoconductive layer provided thereon and then etching to selectively remove nonimage portions of the photoconductive layer.

## BACKGROUND OF THE INVENTION

There is disclosed in Japanese Pat. O.P.I. Pub. Nos 25477/1983, 80659/1983 and the likes, for example, a method for manufacturing a planographic printing plate from a light-sensitive planographic printing plate, comprised of a metal support such as an aluminum plate and a photoconductive light-sensitive layer coated thereon, by steps of forming toner images on the photoconductive layer through the electrophotographic process and removing the nonimage portion in the subsequent etching process using an etchant which is an aqueous alkaline solution.

The above technique attracts much attention because it requires no film original for exposure and thereby allows direct plate making to be practiced. In practicing this technique, there is used a printing plate prepared by coating a photoconductive light-sensitive layer comprised usually of a resin, such as a phenol resin, dispersing in it an organic pigment type photoconductor, particularly a photoconductive light-sensitive layer comprised of a novolac resin dispersing in it copper-phthalocyanine, on a conductive metal support. The removal of the nonimage portion is carried out by dissolving it out with an alkaline etchant through one of various method common in principle to conventional developing methods for processing the so-called PS plates or waterless planographic printing plates which require a film original.

However, these conventional etching methods cannot be always employed as they are, in etching planographic printing plates by the electrophotographic process. And there are, as yet, unsolved problems characteristic of the processing of planographic printing plates through the electrophotographic process.

When the electrophotographic process is used, a trouble liable to arise in the etching process is responsible for the so-called side etching. In processing a planographic printing plate with the electrophotographic mode, nonimage portions of a photoconductive layer are removed in the etching process using a toner image formed on the photoconductive layer as a resist. In this case, the etchant is liable to penetrate from edges of the toner image into the photoconductive layer located under the toner image and remove the edges eventually; therefore, the ink receiving portion corresponding to the image portion of prints becomes smaller than the toner image, and lines of an image printed using such a planographic printing plate become thin. Especially in color printing, halftone reproducibility is lowered and thereby color reproduction becomes liable to cause troubles.

However, when the removal is carried out under conditions to minimize side etching as a measure to avoid the above trouble, the removal of the nonimage portion becomes insufficient, and thereby stains are liable to occur in prints.

Because of the repugnance between the two requirements stated above, it is difficult to control the extent of side etching at a certain intermediate value, and when the continuous treatment of a large amount of printing plates in an automated treating apparatus is taken into consideration, it is very difficult in practice to carry out the treatment while controlling the amount of side etching.

## SUMMARY OF THE INVENTION

The present inventors have made a close study on the etching treatment of planographic printing plates through the electrophotographic process; some of the outcomes are proposed, for example, in Japanese Pat. O.P.I. Publication. No. 32890/1990 as a measure to counter the above problem, and the present invention forms part of such a study, too. Accordingly, a first object of the invention is to provide an improved method for manufacturing planographic printing plates in the electrophotographic mode which can solve the problem of side etching, a second object of the invention is to provide an improved method for manufacturing planographic printing plates in the electrophotographic mode which works effectively in expanding the elution latitude.

The method for manufacturing a planographic printing plate of the invention is characterized in (1) that a toner image is formed in a size larger than that of an original image, in a method for manufacturing a planographic printing plate comprising the steps of forming a toner image in the electrophotographic mode on a light-sensitive planographic printing plate having an electrically conductive support and a photoconductive layer provided thereon, and then removing nonimage portions of the photoconductive layer on which a toner image is

not formed, or in (2) that the toner removing process is carried out after the nonimage portion of the photo-conductive layer is removed.

## DETAILED DESCRIPTION OF THE INVENTION

5

To remove the defects caused by side etching, the present invention adopts a technique to form a toner image in a size larger than that of the original image, at the time of forming the toner image on a light-sensitive planographic printing plate. In other words, the toner image is formed in an enlarged size so as to have at least one enlarged portion around the edge of the original image; that is, the toner image is fattened at least in one direction. Whether the toner image is composed of characters, lines or halftones, it is not necessary to enlarge or fatten the whole edge of the toner image in all directions. For example, the enlargement or fattening only in a certain direction can satisfactorily achieve the object of the invention. Particularly for a halftone image of a shadow portion, the enlargement is not made in all directions for fear of damaging the halftone. In this case, only the shape of the halftone is changed to make the area of the toner image larger than that of the halftone (a square, for example) of the original image.

10

15

"The original image" used here means an artwork original used in an ordinary printing process, an image formed on an original of positive or negative silver halide photographic film or paper, a digital image of computer controlled data and an image displayed on CRT.

20

An original image of a digital image includes an original font data of a character, a data of a line read by a scanner, a halftone image which is read by a scanner and output by a dot-generator, and an image converted properly according to a printing matter.

25

As methods for enlarging a toner image, various techniques are used in the aspects of medium on which original images are formed and means to form toner images. Examples thereof include (1) control of the developing process such as adjustment of bias potential or processing time, (2) dry etching or image treatment on original films in contact exposure of original films, (3) adjustment of exposure and image treatment on originals in exposure with a camera, and (4) image processing such as adjustment in a scanning direction or in a sub-scanning direction, adjustment of output of halftone data converted from original images with a look-up table (hereinafter referred to as LUT), as well as increase in beam diameter or in quantity of light in reversal processing, in the case of digital images using a laser or a LED.

30

Any of the above techniques can be adopted, but the biggest merit of manufacturing a planographic printing plate through the electrophotographic process lies in that it enables the so-called computer to plate process, in which digital images can be directly recorded on the printing plate. In such a plate making process, it is preferable that an electrophotographic latent image be subjected to enlarging treatment. The enlarging treatment can be carried out by a method which processes and converts digital information of an image and then outputs it, or by a method which does not convert such digital information till it is converted with an optical system at the stage of output. Examples of the former method include the following methods and combinations thereof, but use of other methods is not excluded.

35

(1) A method of enlarging an original image by adjusting the modulation timing in the scanning direction.

40

In this method, the controllable range is not limited to one dot, and the control can be made to the extent of less than one dot by selecting a proper timing of the clock.

(2) A method of taking in, as an image, pixels which are in contact with an original image in the sub-scanning direction.

(3) A method of adjusting output halftones through a LUT or the like, this is used when an original image is comprised of halftones.

45

Examples of the enlargement by the above methods (1) and (2) are shown in Fig. 1. In the figure, the area filled with right-hand oblique lines means an original image, and that filled with left-hand oblique lines shows the enlargement by one dot in main scanning direction due to (1) and that by one dot in the sub-scanning direction due to (2).

50

When these methods are employed, conversion has to be made correspondingly to the halftone density so as to form an ideal resist image on a plate taking notice of a dot gain caused in printing, because side etching proceeds uniformly in every portion. In the case of color printing, it is preferable that the conversion curve used be changed for each of yellow, magenta, cyan and black.

55

Further, there can also be used a method comprising the steps of outputting an image on a monochromatic photographic film or paper by use of image data converted by the above method and then reading the image with such an image reading device as is used in a facsimile.

In case a toner image is brought into contact with a neighboring image by the enlargement and thereby the images are eventually damaged, the following measures are taken.

(1) When the space between images is one dot, the images are not enlarged.

(2) When the space between images is two dots, one of the images is enlarged by one dot.

(3) When the enlargement cannot be made in either the main scanning direction or the sub-scanning direction in the above (1) and (2), the image is enlarged on the other side in the same direction.

(4) Fig. 2 shows a procedure to enlarge a shadow portion: when the enlargement cannot be carried out at any portion because the space between halftones in the shadow portion is only one scanning line and completely lost by the enlargement, a portion of the image is made nonimage portion as shown in (B).

The above digital image processing for enlarging a toner image can be applied to either the normal development in which toners are adhered to unexposed portions or the reversal development in which toners are adhered to exposed portions.

In the reversal development, a toner image can be enlarged by raising the luminous intensity or expanding the beam diameter of a laser or a LED. Besides such a direct recording method, the enlargement of a toner image can also be carried out by controlling the exposing condition in contact exposure of a positive or negative film original or in projection exposure from an artwork original. These methods can be carried out as follows:

(1) Contact exposure of positive film (normal development)

An enlarged image is formed on a positive film by increasing the exposure or employing a spacer in the stage of making a positive film through contact exposure of a negative film. In the case of a digital image, a positive film having an enlarged image can be prepared by drawing an image subjected to enlargement processing with a plotter. This technique can be practiced by drawing an enlarged image on a negative film and preparing a positive film from that.

(2) Contact exposure of negative film (reversal development)

An enlarged latent image can be obtained by simply increasing the exposure or employing a spacer.

(3) Projection exposure from positive artwork original (normal development)

An enlarged image is formed on a positive photographic paper in the same procedure as in (1).

(4) Projection exposure from negative artwork original (reversal development)

An enlarged image is formed in a procedure to increase the exposure or the like.

The above methods are to adjust a toner image by changing the size of its electrophotographic latent image through exposure. In addition to these methods, a toner image can also be enlarged by adjusting the bias potential in a processed portion, the space between processing electrodes or the processing time, or adjusting the characteristics of a developer or a photoconductive layer, or by adhering toners through pressing or fusing in the toner fixing process.

While the amount of side etching depends on the number of screen lines and the halftone reproducing range desired in a print, it is equal to the sum of minimum side etching amount 5 corresponding to the thickness of photoconductive layer 2 and intended side etching amount 6, as illustrated in Fig. 3. Minimum side etching amount 5 is equal to the thickness of photoconductive layer 2, and a side etching amount less than this thickness makes it difficult to remove nonimage portions of the photoconductive layer and thereby produces undesirable results. The thickness of the photoconductive layer is usually 0.5 to 30  $\mu$ . To maintain a proper resolution after etching, the thickness of this photoconductive layer is not more than 10  $\mu$ , and to maintain a proper printing durability and sensitivity, the thickness is preferably not less than 1  $\mu$ . To increase the amount of side etching, there can be adopted a means to raise the activity of an etchant or to lengthen the etching time.

Preferably, a resist image composed of a photoconductive layer, which functions as an ink receiving layer, is smaller than original image 4. Therefore, the side etching is deliberately allowed to progress exceeding minimum side etching amount 5 (corresponding to the thickness of photoconductive layer 2) usually by 0 to 30  $\mu$ , preferably by 5 to 15  $\mu$ , in order to obtain intended side etching amount 6. Setting the intended side etching amount at such a value has effects on preventing adhesion of residual components of the photoconductive layer as well as absorbing the fluctuation in etchant activity.

The reason for setting a resist image smaller than an original image 4 (reduction of an original image) lies in that dot gains in printing are taken into consideration. Accordingly, a toner image and a side etching amount are adjusted so as to give intended side etching amount 6 by allowing the side etching to proceed across the periphery of original image 4 within a range of 0 to 20, preferably 5 to 10  $\mu$ .

It has been found, through experiments, that though image reproducibility is kept well even when an image

is enlarged with an intended side etching amount of 0  $\mu$ , the frequency of stain in prints obtained with a so-prepared printing plate is larger than that with a printing plate subjected to a proper intended side etching.

The enlargement of a toner image is carried out in an amount within the range of 0.5 to 40  $\mu$ m, and preferably 1 to 15  $\mu$ m. The minimum side etching amount, d, intended side etching amount, D reduction amount of an original image, 1 and enlargement amount of a toner image, L have the following relation;

$$L = d + D - 1$$

Next, the reason why intended side etching amount 6 is set as above is described using Fig. 4. In Fig. 4 showing halftone reproducibility, the halftone dot reproducing curve is given by B when the reproducibility is exactly corresponding to the halftone dot density of an original image. In the invention, however, the toner image is set to give curve A which is obtained by adding dot gains to curve B, and the side etching amount is set to give a halftone reproducibility of curve C to a resist image consisting of a photoconductive layer in the etching process; therefore, dot gain occurs in printing and thereby the printed image is reproduced to give curve B. Even when a toner image is set to give curve B and etching is carried out to give curve C by a conventional method, prints obtained are not immune from stains in nonimaged portions and damage in shadows. Further, even when etching is performed by setting a reproducing curve having a dot loss larger than that in curve C, a faithful printing to give curve B cannot be obtained.

The reproducibility contained in the present invention may be any one as long as it meets the requirement of A>B (straight line) in Fig. 4 and, therefore, C is allowed to coincide with B.

The reproduction curves of halftone dot, A and C vary depending upon screen line number. The halftone dots of 5%, 50% and 95% in an original image B are preferably converted to 6 to 20%, 55 to 75% and 96 to 99.9% in A, respectively, and 2 to 4%, 35 to 45% and 90 to 94% in C, respectively.

The conception of the reproducing curve described above can be equally applied to characters and line drawings.

Planographic printing plates to which the present invention is applied have a photoconductive layer containing, as an organic photoconductor, a photoconductive pigment and/or a photoconductive material having a solvent capable of completely dissolving the material itself (a soluble photoconductor) mixed in a binder resin. The effect of the invention can be best demonstrated in planographic printing plates having a photoconductive layer using an organic photoconductor of pigment type. Examples of such an organic photoconductive pigment include those perylene pigments, quinacridone pigments, bisbenzimidazole pigments, aromatic polycondensed ring compounds, monoazo pigments, disazo pigments, trisazo pigments, metallic or nonmetallic phthalocyanine pigments and zinc oxide which are described in Japanese Pat. Exam. Pub. Nos. 2780/1965, 12671/1969, 30035/1971, 16474/1969, 30513/1973, 7434/1975 and Japanese Pat. O.P.I. Pub. Nos. 18543/1972, 18544/1972, 30330/1972, 37543/1972, 11136/1974, 99142/1974, 109841/1976, 134632/1979, 11715/1980, 105254/1980, 153948/1980, 161250/1980, 1944/1981, 2352/1981, 9752/1981, 19063/1981, 29250/1981, 69644/1981, 50050/1981, 125751/1984, 176756/1984, 17751/1985, 17752/1985, 17753/1985, 17754/1985, 17755/1985, 17756/1985, 17757/1985, 17758/1985, 17759/1985, 17760/1985, 17761/1985, 17762/1985, 35750/1985, 67869/1986, 67870/1985. Of the above organic photoconductive pigments, phthalocyanine pigments can best bring out the effect of the invention when used in the photoconductive layer of a planographic printing plate.

As binder resin for the photoconductive layer of light-sensitive planographic printing plates according to the invention, a high molecular compound soluble or dispersible in the above etchant is preferred.

Usable binder resins are, for examples, copolymers of an acrylate, a methacrylate, styrene or vinyl acetate and a monomer containing a carboxyl group or an acid anhydride group, such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, maleic anhydride or fumaric acid. Typical examples thereof include styrene/maleic anhydride copolymers, styrene/monoalkyl maleate copolymers, methacrylic acid/methacrylate copolymers, styrene/methacrylic acid/methacrylate copolymers, acrylic acid/methacrylate copolymers, styrene/acrylic acid/methacrylate copolymers, vinyl acetate/crotonic acid copolymers and vinyl acetate/crotonic acid/methacrylate copolymers. Besides the above, there can also be used copolymers containing methacrylamide, vinylpyrrolidone, monomers having a phenolic hydroxyl group, sulfone group, sulfonamido group or sulfonimido group, phenol resins, partially hydrolyzed vinyl acetate resins, xylene resins and vinyl acetal resins such as polyvinyl butyral.

Copolymers containing units derived from monomers having an acid anhydride group or a carboxyl group as a copolymer component as well as phenol resins are advantageously used, because these can provide a photoconductive layer with a high charge holding property when used in a photoreceptor for electrophotographic process.

Among the copolymers containing units derived from monomers having an acid anhydride group as a copolymer component, copolymers of styrene and maleic anhydride are preferred. Half esters of these copolymers can also be favorably used. Among the copolymers containing monomers having a carboxyl group as a

copolymer component, preferred ones are binary or more multiple copolymers of acrylic acid or methacrylic acid and alkyl esters, aryl esters or aralkyl esters of acrylic acid or methacrylic acid. In addition, copolymers of vinyl acetate and crotonic acid as well as terpolymers of vinyl acetate, vinyl ester of a carboxylic acid having 2 to 18 carbon atoms and crotonic acid are also preferable examples. Among the phenol resins, the preferred

are novolac resins prepared by allowing phenol, o-cresol, m-cresol or p-cresol to react with formaldehyde or acetaldehyde under acid conditions. These binder resins may be used singly or in combination of two or more types.

Typical examples of the above phenol resin include those prepared by condensing at least one substituted phenol selected from phenol, o-cresol, m-cresol, p-cresol, ethylphenol, isopropylphenol, t-butylphenol, t-amylphenol, hexylphenol, t-octylphenol, cyclohexylphenol, 3-methyl-4-chloro-6-t-butylphenol, isopropylcresol, t-butylcresol, t-amylcresol, hexylcresol, t-octylcresol and cyclohexyl cresol with an aliphatic or aromatic aldehyde such as formaldehyde, acetaldehyde, acrolein, crotonaldehyde or furfural. Further, polyhydroxyphenyl resins prepared by polycondensation of pyrogallol or resorcinol and acetone can also be used.

Among these phenol resins, preferred ones are novolac type phenol resins prepared by condensing at least one of phenol, o-cresol, m-cresol and p-cresol with formaldehyde or acetaldehyde under acid conditions.

The average molecular weight of these phenol resin is 350 to 20,000, preferably about 300 to 6,000. It is preferable that these phenol resins be soluble in organic solvents such as ketones including acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, glycol ethers including ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, dioxane, and esters including butyl acetate, ethyl acetate.

In one example of preparing a planographic printing plate substrate to which the present invention, 1 part of a photoconductive material and 0.01 to 100 parts (preferably within the range where the photoconductive layer is dissolved and removed in an alkaline solution) of a binder phenol resin are mixed in one of the above organic solvents and, when necessary, an electron accepting compound or an electron donating compound is added in an amount of 0.01 to 100 moles per mole of pigment (preferably 0.01 to 10 moles), then the mixture is uniformly dispersed by use of a ball mill or a supersonic disperser. The light-sensitive solution obtained is coated and dried to a thickness of 1 to 50  $\mu\text{m}$ , preferably 1 to 10  $\mu\text{m}$ , on a conductive support described later, followed by a heat treatment at 70 C or above to raise the solubility of the photoconductive layer in the solution to remove the photoconductive layer.

As supports for planographic printing plates according to the invention, there can be employed conductive supports having a hydrophilic surface such as aluminium plates, resin sheets laminated with aluminium, zinc plates, bimetal plates including copper-aluminium plates, copper-stainless steel plates, chromium-copper plates, and trimetal plates including chromium-copper-aluminium plates, chromium-lead-iron plates, chromium-copper-stainless steel plates.

It is preferable for supports having an aluminium surface to be subjected to a surface treatment such as roughening, anodizing or dipping in an aqueous solution of sodium silicate, potassium zirconium fluoride or a phosphate. In addition, there can also be used favorably aluminum plates roughened and then dipped in an aqueous solution of sodium silicate as disclosed in U.S. Pat. No. 2,714,066; and aluminium plates anodized and then dipped in an aqueous solution of an alkali metal silicate as disclosed in Japanese Pat. Exam. Pub. No. 5125/1972. The anodizing can be carried out by applying an electric current, using an aluminium plate as anode, to an electrolytic solution comprised of a single or combination of aqueous or nonaqueous solutions of inorganic acids such as phosphoric acid, chromic acid, sulfuric acid, nitric acid, organic acids such as oxalic acid, sulfamic acid, or salts of them.

Other useful surface treatments include the silicate electrodeposition disclosed in U.S. Pat. No. 3,658,662 and the treatment with polyvinyl phosphonic acid disclosed in German Offenlegungsschrift No. 1,621,478.

The purpose of these surface treatments is to make the surface of the support hydrophilic and, further, to prevent harmful reactions between the support and the photoconductive layer provided thereon and to improve the adhesion between them.

In the invention, there may be provided, when necessary, an alkali-soluble intermediate layer comprised of casein, polyvinyl alcohol, ethyl cellulose, phenol resin, styrene-maleic anhydride copolymer or polyacrylic acid between the conductive support and the photoconductive layer, for the purposes of raising the adhesion between these two and improving electrostatic properties in the exposure process.

Further, an overcoat layer to be dissolved at the time of removing the photoconductive layer may be provided on the photoconductive layer of light-sensitive planographic printing plates according to the invention, in order to improve the electrophotographic property of the photoconductive layer, the developing characteristics in toner development, and the image characteristics.

It is preferable that developers (toners) used in the method of the invention be hydrophobic and ink-receptive and contain a high-molecular compound selected from polystyrene type resins, polyester type resins (e.g.,

acrylic esters containing amino groups, long-chained acrylic esters), acrylic type resins (e.g., resins containing phenolic hydroxyl groups or sulfone groups), epoxy resins, vegetable-oil-modified alkyd resins, cyclized rubbers, asphalt and polyvinyl chlorides. In addition, there may be contained, within the limits not harmful to the granulation property and fixability of a toner, a colorant such as carbon black, Nigrosine pigment, Carmine 6B, phthalocyanine blue, benzidine yellow or phthalocyanine green and, further, a charge controlling agent such as a metal salt of fatty acid or naphthenic acid, a metal-containing pigment or a sulfonate.

The means to form a toner image in the electrophotographic mode is not particularly limited, and conventional means can be adopted. However, it is preferable that the toner development be performed in an electrophotographic liquid developer comprised of an electrical insulating liquid carrier containing a colorant (e.g., carbon black, copper phthalocyanine), a coating agent and a charge controlling agent. Particularly preferred developers are those which contain, besides a colorant, one or plural types of polyethylene, polypropylene, ethylene copolymer and propylene copolymer as coating agents, and a phosphate type surfactant as a charge controlling agent.

Etchants used in the method according to the invention contain a strong alkaline aqueous solution having a pH value of 12 or more, which is comprised of an alkali metal hydroxide, an alkali metal silicate, an alkali metal phosphate or an alkali metal aluminate, water and, if necessary, a surfactant and other additives.

Further, etchants used in the method according to the invention contain an aqueous solution comprised of an anionic surfactant, an organic solvent of which solubility to water is 10 wt% or less, an alkali agent, water, and, if necessary, an antistain agent as described, for example, in Japanese Pat. O.P.I. Pub. Nos. 77401/1976, 80228/1976, 44202/1978 and 52054/1980. Furthermore, there can also be used a double purpose developer for negative PS plates and positive PS plates described, for example, in Japanese Pat. O.P.I. Pub. No. 130741/1985.

In order to improve the coatability, the surface tension of an etchant is adjusted at 45 dyne/cm or less, preferably 35 dyne/cm or less, with the addition of a surfactant.

Usable rinsing solutions include water and aqueous solutions containing an alkali agent, besides ones disclosed in Japanese Pat. Appl. No. 17835/1991. When etching and rinsing are carried out continuously, it is needless to say that the rinsing solution becomes alkaline because the etchant is brought into the rinsing process.

In the printing process, there occasionally appear stains attributable to toners; therefore, it is preferable to remove such toners prior to printing.

Removal of toners can be performed, for example, by the methods disclosed in Japanese Pat. O.P.I. Pub. Nos. 66863/1981, 130766/1981, 280769/1987, a method for wiping out toners using an aqueous organic solvent (preferred organic solvents are alcohols whose solubility to water is 10 wt% or less at 20 C, combination with a surfactant gives favorable results), and a method for wiping out toners using a treating agent comprised of a hydrocarbon solvent dispersed in water.

## EXAMPLES

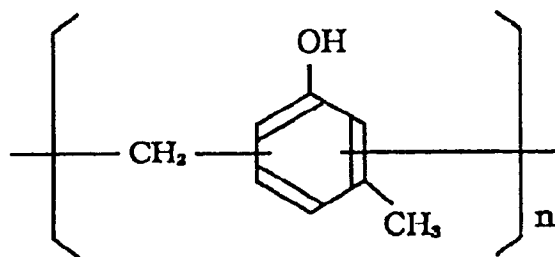
The present invention is hereunder illustrated with examples. "Part" in the examples is by weight unless otherwise indicated.

### Example 1

#### A. Preparation of light-sensitive planographic printing plate

In 20 parts of propylene glycol monomethyl ether were dissolved 3 parts of phenol resin having the following structure and 0.1 part of maleic anhydride. After 1 part of Lionol Blue ER ( $\epsilon$  type copper phthalocyanine) made by Toyo Ink Co. was added thereto, the mixture was dispersed for 30 minutes using glass beads to obtain a dispersion. Separately, a 1,100 mm x 400 mm aluminium plate was roughened by electrolytic etching in a hydrochloric acid bath, followed by anodizing and sealing with hot water. Subsequently, the dispersion was coated and dried on the plate so as to give a dry thickness of 5  $\mu$ m. Thus, a light-sensitive planographic printing plate was obtained.

5



10

Average molecular weight: 1500

#### B. Formation of latent image

15

After charging the above planographic printing plate to a surface potential of +200V, a nonimage portion was subjected to scanning exposure to form an electrophotographic latent image, by use of a plotter capable of writing in the semiconductor laser mode with a resolution of 2000 DPI. This plotter was to record an image (an electrostatic latent image) according to the image signal sent from a computer connected. The power of the laser beam at the plate surface was 1 mW, and the beam diameter was 13  $\mu$  at the point where the light intensity being  $1/e^2$  of the maximum value.

20

The electrophotographic latent image was enlarged in the following procedure.

For line drawings and characters, enlargement was made by one dot around the periphery of the original image. For halftone dot images, LUT conversion was made as indicated by reproducing curve A of Fig. 4. Through this LUT conversion, halftone dot densities of 5%, 50% and 95% on the original image were converted

25

into 9%, 59% and 98%, respectively.

#### C. Developing and fixing of latent image

30

The space between the developing electrodes was set at 2 mm all over the electrode surfaces. A bias potential of +40 V was applied onto the surface of the photoconductive layer of the plate, and developing was performed for 7 seconds while continuously feeding a liquid developer to the electrode tube at a flow rate of 10 l/min. Then, fixing was carried out for 5 seconds by heating the plate to 150°C with an infrared heater.

The liquid developer used was prepared in the following manner.

35

10% Isopar G solution of octadecyl methacrylate/

methacrylic acid copolymer (90:5) 10 parts

40

MA-100 (carbon black made by Mitsubishi Kasei Corp.)

1 part

The above mixture was dispersed for 5 hours using glass beads.

45

Subsequently, 1 part of Sanwax 151 P (polyethylene made by Sanyo Chemical Ind., average molecular weight: 2000) was added to the resultant mixture, and was dispersed for another 3 hours while keeping at 80°C. The dispersion was then diluted to 80 times its volume to obtain the liquid developer.

#### D. Etching

50

The light-sensitive planographic printing plate, on which toner images were formed as above, was etched to remove a nonimage portion in an etching apparatus (see Japanese Pat. Exam. Pub. No. 60825/1988) with a carrier width of 1150 mm illustrated in Fig. 1 of Japanese Pat. Appl. No. 171648/1991.

The amount of side etching was set at 10  $\mu$  by adjusting the etching time.

55

The composition of the etchant was as follows. It was diluted with water at a volume ratio of 1:5 (water) before use.



	Benzyl alcohol	6.0 parts
	Propylene glycol	6.0 parts
5	p-t-Butyl benzoic acid	5.0 parts
	Benzoic acid	2.0 parts
	2-Hydroxy-3-naphthoic acid	2.0 parts
10	50% KOH aqueous solution	26.3 parts
	Potassium silicate aqueous solution (SiO <sub>2</sub> :26 wt%)	
15	(potassium silicate A made by Nippon Chemical)	
		29.0 parts
	Pelex NBL (sodium alkylnaphthalene sulfonate	
20	made by Kao Atlas Co.)	0.2 part
	Ethylenediaminetetracetic acid	0.3 part
25	Water	24.0 parts

The above diluted etchant was kept at 27°C and fed to the surface of the developed plate at a rate of 400 ml/min. The carrier speed of the plate was adjusted so as to give an etching time of 15 seconds.

The amount of the etchant applied onto the printing plate was adjusted at 180 ml/m<sup>2</sup>.

30 Prior to printing, toners present on the surface of the printing plate were wiped out with a sponge wiper soaked with Isopar G made by Exxon Co.

In the procedure described above, 100 plates were continuously processed to examine adhesion of light-sensitive layer components to non-image portions of the plate, resist images on the plate, image reproducibility in printing, and occurrence of stains in nonimage portions during printing. The method according to the invention gives excellent printing plate in good qualities; equally good results were achieved in prints, that is, fine lines and halftones were well reproduced, and no stains were observed in nonimage portions. The results are shown in Table 1.

#### Other Examples and Comparative Examples

40 Experiments were made using various toner image enlarging procedures described in the following paragraphs and Table 1.

In Examples 2 and 3, enlargement of characters and line drawings was performed by enlarging their electrophotographic images by one dot each in the scanning direction and the sub-scanning direction, and setting the LUT and the side etching width as shown in Table 1.

In Example 4, LUT conversion was made, in the area where the halftone reproducibility was 90%, so as to have the number of screen lines coincide with that shown in Fig. 5.

In Examples 5, 6 and Comparative Example 5, imagewise exposure was conducted and then reversal processing was performed using Power Toner made by Cemmco Co. as liquid developer, besides the conditions described in Table 1. In Example 6, the diameter of the laser beam was adjusted to be 18 μ at the point where the light intensity was 1/e<sup>2</sup> of the maximum value.

In Example 7, printing plates carrying fixed toner images were etched in the apparatus illustrated in Japanese Pat. Exam. Pub. No. 60825/1988 as in Example 1. As etchant, there was used one prepared by diluting 1 liter of SDR-1 made by Konica Corp. with 5 liters of water and adjusting to 30°C. As a rinsing solution, water was used.

After setting the etching time so as to give a side etching width of 15 μ, 200 plates were continuously processed while compensating 40 ml of a diluted etchant (Konica Corp.'s SDR-1R was diluted to 4 times its volume with water) for each plate.

The minimum side etching width and the maximum side etching width obtained in this Example are shown in Table 1 together with the evaluation results of respective printing plates.

In Comparative Example 6, printing plates carrying fixed toner images, which were used in Comparative Example 1, were continuously processed in the same manner as in Example 7, except that the side etching width was set at 7  $\mu$ .

The procedure of Comparative Example 7 was the same as that in Comparative Example 6, except that the side etching width was set at 15  $\mu$ .

In Example 9, printing free from dot gain was attempted by reducing the amount of ink, but prints obtained were poor in solid density, low even in densities of details and insufficient in image reproducibility.

The evaluation results in the above Examples and Comparative Examples are summarized in Table 1.

#### Example 10

A printing experiment was conducted under the same conditions as in Example 1, except that toners were not removed. In printing the first 300 sheets, deterioration in halftone reproducibility was observed, that is, halftone densities of 5%, 50% and 95% on the original image became 6%, 52% and 96%, respectively. But fine lines were satisfactorily reproduced, and no stains occurred in nonimage portions.

When edges of toner images on the plate were examined with a microscope before printing, it was found that a portion of the toner layer removed from the photoconductive layer by side etching was left on nonimage portions of the support in a shape of fringe. When printing was further kept on, toners gradually came to be transferred from the printing plate to the prints and the color ink became slightly turbid, in the course of printing the next 300 sheets. However, good prints like those in Example 1 were obtained after that.

Table 1-1

	Method for enlarging toner image				Side etching width (μ)	Stain adhesion numbers of light-sensitive layer component to non-image portions (100μ) <sup>2</sup>	Resist image of light-sensitive layer on plate (dot portion) (%)				Reproducibility in printing				
	Character & line drawing	Halftone portion (%)					(original image)	50%	95%	(dot portion) (%)	Range reproduced	Reproducibility of 40μ fine line (μ)			
		5%	50%	95%											
Example 1	Enlarged by 1 dot around the whole periphery			9	59	98		4	41	93	5	50	95	1-98% portion is well reproduced	45
Example 2	Enlarged by 1 dot in scanning direction and sub-scanning direction			6	53	96		4	42	94	5	50	-	1-90%, shadows are slightly damaged	45
Example 3	Enlarged by 1 dot in scanning direction and sub-scanning direction			7	54	97		4	42	94	5	50	95	1-98% portion is well reproduced	40
Example 4	Enlarged by 1 dot around the whole periphery			18	75	99.5		4	41	93	5	50	95	1-98%, but resolution for shadow is slightly lowered	30
Copm. Example 1	Toner image was not enlarged						0	1	33	91	2	39	92	Poor reproducibility, highlight is lost	20
Copm. Example 2	Toner image was not enlarged						20-30	3	41	94	5	50	-	1 to 90%, shadows are damaged	35
Copm. Example 3	Toner image was not enlarged						2-5	3	37	92	4	46	93	Poor color reproduction	30
Copm. Example 4	Toner image was not enlarged						0	0	21	88	0	26	90	Poor color reproduction	0

Table 1-2

	Method for enlarging toner image				Side etching width (μ)	Stain adhesion numbers of light-sensitive layer component to non-image portions (100μ) <sup>2</sup>	Resist image of light-sensitive layer on plate (dot portion) (%)				Reproducibility in printing					
	Character & line drawing		Halftone portion (%)				5%	50%	95%	(dot portion) (%)			Range reproduced	Reproducibility of 40 μ fine line (μ)		
			(original image)							5%	50%	95%				
Example 5	Enlarged by 1 dot around the whole periphery		6	54	97	0	4	41	94	5	50	95	1-98% portion is well reproduced	43		
Example 6	Enlarged by 1 dot around the whole periphery		Not enlarged		0	4	42	96	5	50	97	Ditto	55			
Copm. Example 5	Toner image was not enlarged				10	0	2	35	92	3	45	93	Poor color reproduction	25		
Example 7	Enlarged by 1 dot around the whole periphery		12	66	99	0	3	38	92	4	49	94	1-98% portion is well reproduced	33		
						0	5	43	95	6	51	96	Ditto	45		
Copm. Example 6	Toner image was not enlarged				13	0	0.3	25	89	0.5	30	91	Poor color reproduction	18		
					-	Nonimage portion was not removed, printing was impossible									-	
Copm. Example 7	Toner image was not enlarged				20	0	0	21	88	0	26	90	Poor color reproduction	0		
					10	0	1	33	91	2	39	92	Poor color reproduction	25		
Example 8	Enlarged by 1 dot around the whole periphery		12	67	99	0	3	41	94	5	50	95	1-98% portion was well reproduced	40		
Example 9	Enlarged by 1 dot around the whole periphery		12	67	99	0	5	50	95	7	58	97	Poor color reproduction	45		

\*1) Densities after LUT conversion to halftone densities of original image

\*2) Original image was reproduced in 1-98%.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1: a schematic diagram showing an example of image enlargement

Fig. 2: a schematic diagram showing an example of image enlargement

Fig. 3: a conceptual schema illustrating the method of the invention

Fig. 4: a graph showing halftone reproducibility

Fig. 5: a graph showing the number of screen lines

5

## DESCRIPTION OF THE NUMERICAL SIGNS

1: a support

2: a photoconductive layer

10

3: a toner image

4: an original image

5: a minimum side etching amount

6: an intended side etching amount

15

## Claims

1. A method of preparing a planographic printing plate from a light-sensitive planographic printing plate comprising an electrically conductive support provided thereon with a photoconductive layer comprising a photoconductor and an alkali soluble resin, said layer having a thickness of from 0.5 to 30  $\mu\text{m}$ , said method comprising:  
 charging the photoconductive layer;  
 forming an electrophotographic latent image on the charged layer imagewise from an original image;  
 developing the latent image by applying toner to the exposed layer to form a toner image; and  
 removing with an alkali solution that part of the photoconductive layer on which the toner image is not formed to form a relief image on the support;  
 wherein the toner image is larger than the original image.
2. A method according to claim 1 which further comprises removing toner from the toner image after the part of the photoconductive layer on which the toner image is not formed has been removed.
3. A method according to claims 1 to 2 wherein the toner image is made larger than the original image by optically enlarging the original image.
4. A method according to any one of the preceding claims wherein side-etching of the photoconductive layer is carried out during the removal of the part of the layer on which the toner image is not formed in an amount of not less than the thickness of the photoconductive layer.
5. A method according to claim 4 wherein the side-etching is carried out in an amount of from the thickness  $d$   $\mu\text{m}$  of the photoconductive layer to  $(d + 30)$   $\mu\text{m}$ .
6. A method according to any one of the preceding claims wherein the photoconductor is a phthalocyanine pigment.
7. A method according to any one of the preceding claims wherein the alkali soluble resin is a phenol novolak resin.
8. A method according to any one of the preceding claims wherein the toner image is 0.5 to 40  $\mu\text{m}$  larger than the original image in at least one direction or in all directions.
9. A method according to any one of the preceding claims wherein the relief image is smaller than the original image.
10. A method according to any one of the preceding claims wherein the imagewise exposing is carried out using a laser beam outputting digital data converted from the original image.
11. A method according to claim 10 wherein the digital data has been converted from a dot image of the original image.

12. A method according to claim 11 wherein the size of the dots in the relief image is smaller than that of the original image.

5 13. A method according to any one of claims 10 to 12 wherein said imagewise exposing is carried out using a screen line number which 10 to 60% lower at a shadow part having a dot density of not less than 90% than at the other dot density part.

10

15

20

25

30

35

40

45

50

55

FIG. 1

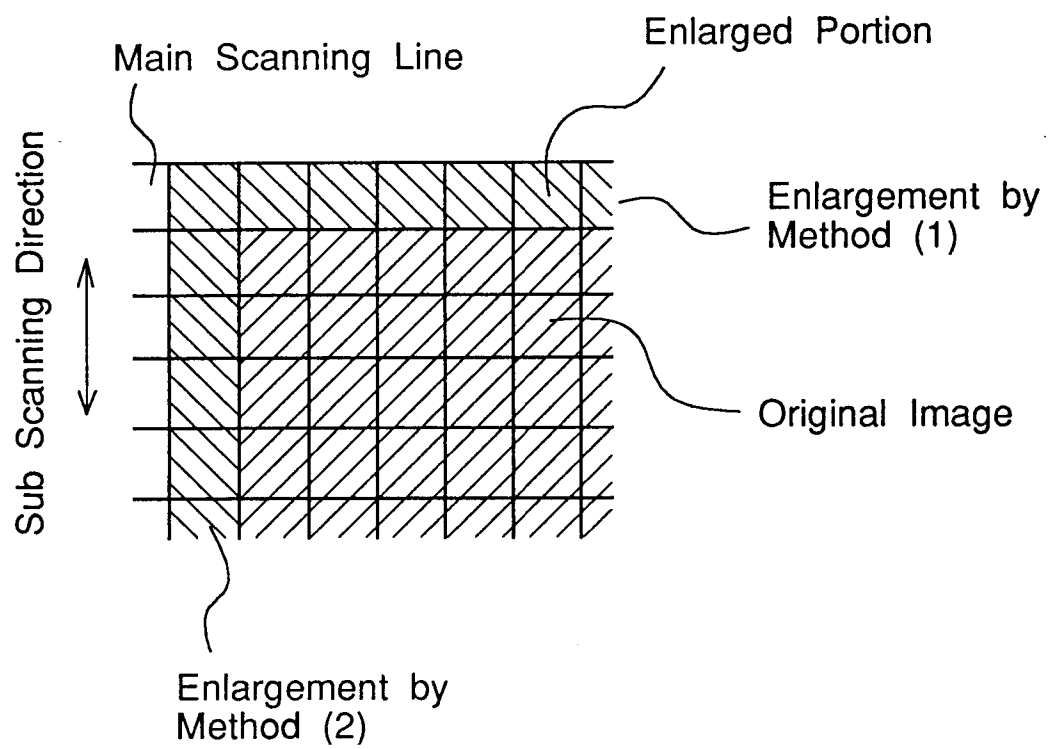


FIG. 2

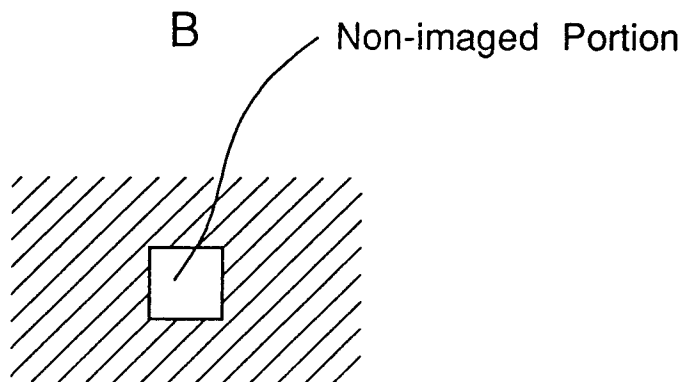
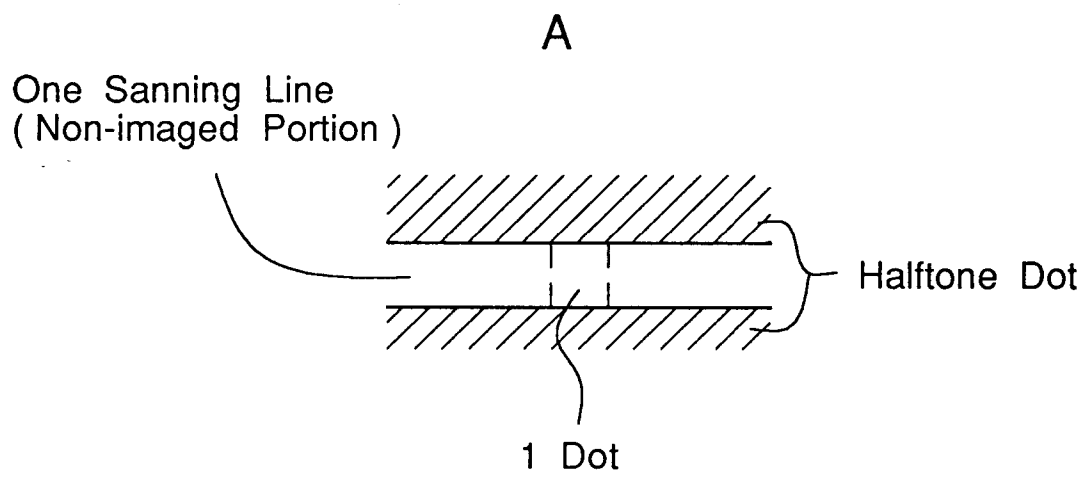




FIG. 3

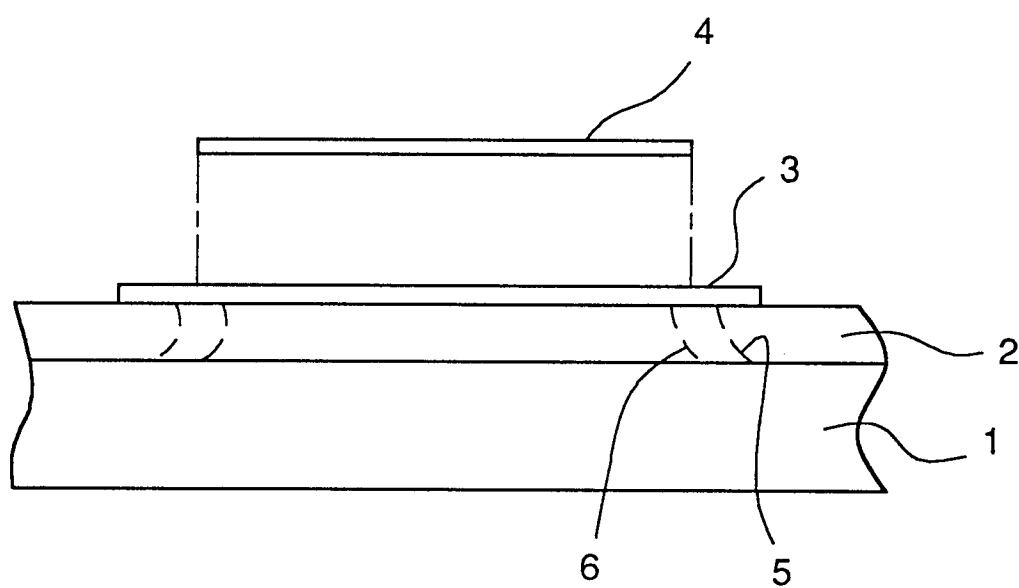


FIG. 4

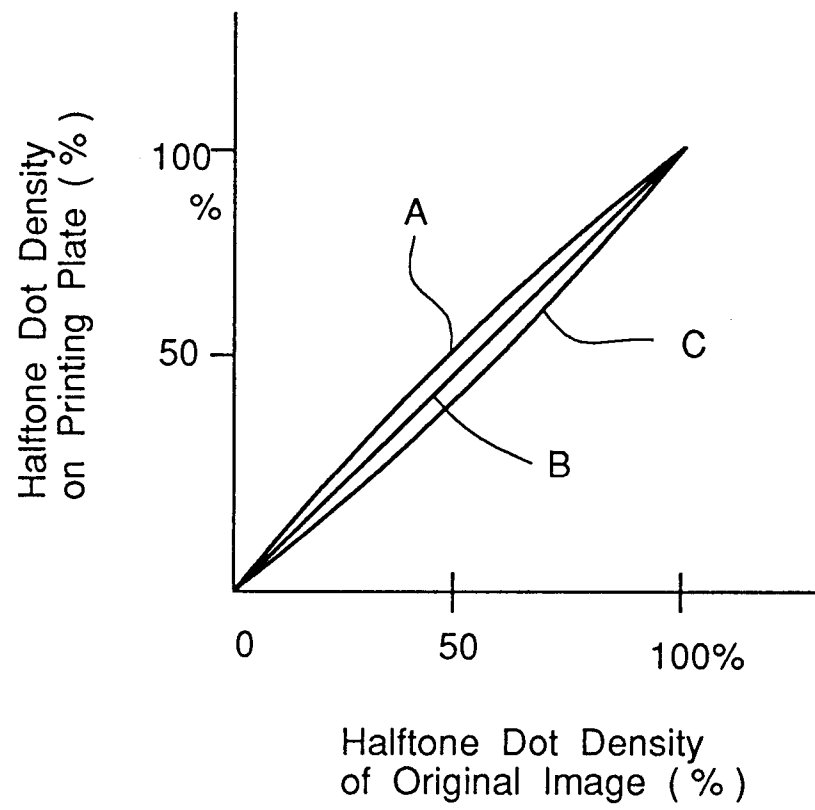
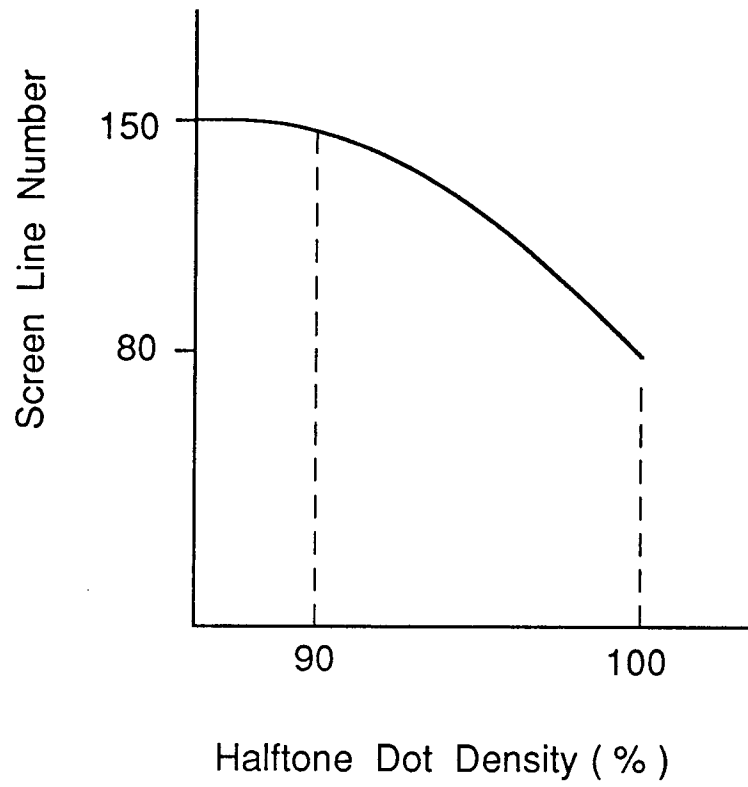


FIG. 5





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5857

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-3 300 244 (MITSUBISHI PAPER MILLS, LTD.) * page 12, line 3 - line 5; claims 1-8 *	1-13	G03G13/28
A	--- JAPANESE PATENTS GAZETTE Week 8416, 30 May 1984 Derwent Publications Ltd., London, GB; Page 17, AN 84-098190/16 & JP-A-59 044 060 (MITSUBISHI PAPER MILLS) 12 March 1984 * abstract *	1-13	
A	--- PATENT ABSTRACTS OF JAPAN vol. 010, no. 207 (M-500)19 July 1986 (KONISHIROKU PHOTO IND., CO., LTD. ) 11 March 1986 & JP-A-61 049 895 * abstract *	1-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 SEPTEMBER 1992	Examiner HINDIAS E.
<p><b>CATEGORY OF CITED DOCUMENTS</b></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 ..... &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 01.82 (P0401)