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Tsuboi et al.

[11] **3,901,706**
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[54] PHOTO-PLATEMAKING PROCESS AND APPARATUS THEREFOR

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[52] **U.S. Cl.** .... **96/33;** 96/29 L
[51] **Int. Cl.**^{2} **G03F 7/02**
[58] **Field of Search** .... 96/29 L, 33

[56] **References Cited**

UNITED STATES PATENTS

2,448,861	9/1948	Colt	96/33
2,494,053	10/1950	Mitson et al.	96/33
3,385,701	5/1968	Ormsbee et al.	96/29 L
3,511,656	5/1970	Regan et al.	96/29 L
3,620,737	11/1971	Etter	96/33
3,625,687	11/1971	Dunkle	96/33
3,814,602	6/1974	Shinozaki et al.	96/29 L
3,814,603	6/1974	Mukaido et al.	96/29 L

OTHER PUBLICATIONS

Hartsuch, P. D., Chemistry of Lithography, (1961), Reprinted 1963, LTF, Inc., New York, N.Y., pp. 152 & 153.

West Germany, OLS 2,048,594, April 1971, Mukaida et al., 23 pp. spec., 2 sh. dwg.

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[57] ABSTRACT

A photo-platemaking process for making a printing plate and apparatus for accomplishing the process.

The photo-platemaking process comprises the steps of (1) image-wise exposing a plate substance for making a photo-plate which consists of a hydrophilic surface part or a hydrophilic layer provided on an oleophilic support and containing therein silver depositing nuclei for diffusion transfer, a silver halide emulsion layer being superimposed thereon; (2) developing the same to form a positive silver image on the hydrophilic surface part or on the hydrophilic layer; (3) washing with water to remove the silver halide emulsion layer; (4) subjecting the hydrophilic surface part or the hydrophilic layer to an etch-bleaching treatment to thereby expose the oleophilic surface part which corresponds to the silver image; and (5) subjecting the assembly to after-treatment whereby any residue deteriorated due to the etch-bleaching treatment is rendered fragile for removal.

The apparatus for photo-platemaking consists of: (a) a plurality of twin rollers to convey the plate substance for making a planographic printing plate; (b) a developing trough, a washing trough, an etch-bleaching trough and an after-treating trough for accomplishing the corresponding treatments of the plate substance; (c) means for removing the silver halide emulsion layer in the washing trough, and (d) means for removing the etch-deteriorated residue in the after-treating trough.

The present apparatus may be combined with a photographing device comprising: (i) a manuscript supporting bed; (ii) a magnification controlling device for determining the position of a photographic lens according to the photographic magnification desired; (iii) a camera to photograph a manuscript on the plate substance (which has been housed in a magazine) by means of the lens; and (iv) means to convey the photographed plate substance in the form of a roll to a photoengraving device and means to cut off the conveyed part in order to automatically and continuously perform the photographing operation and the photo-platemaking operation.

14 Claims, 3 Drawing Figures

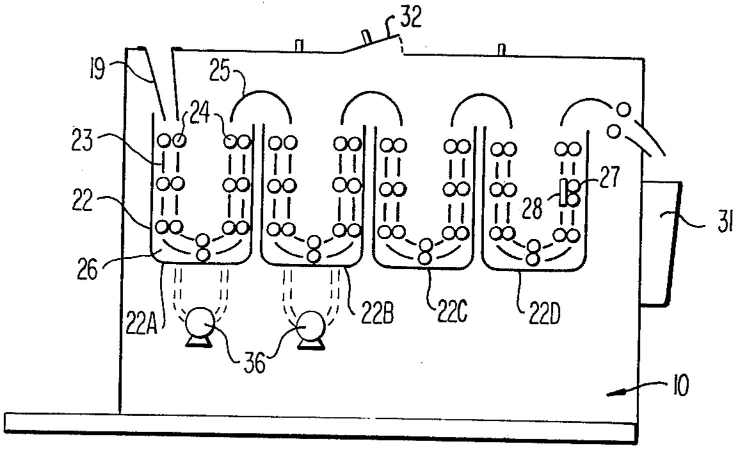

FIG I

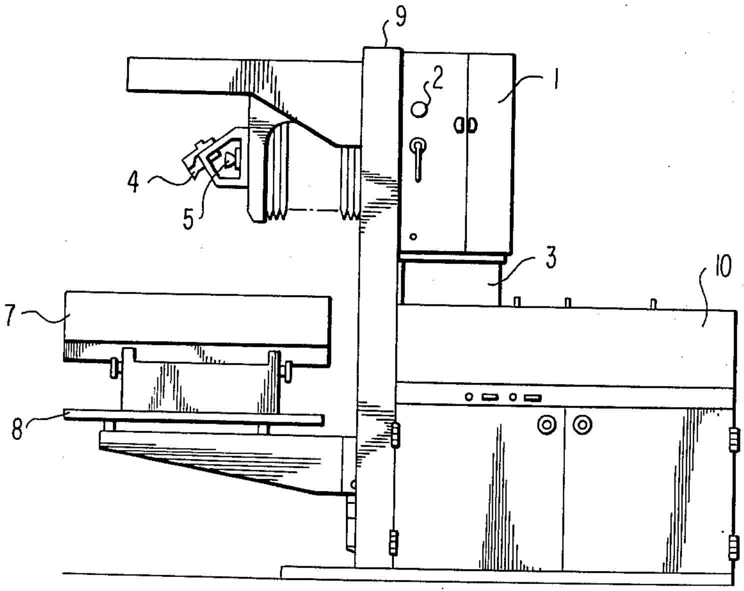

FIG. 2

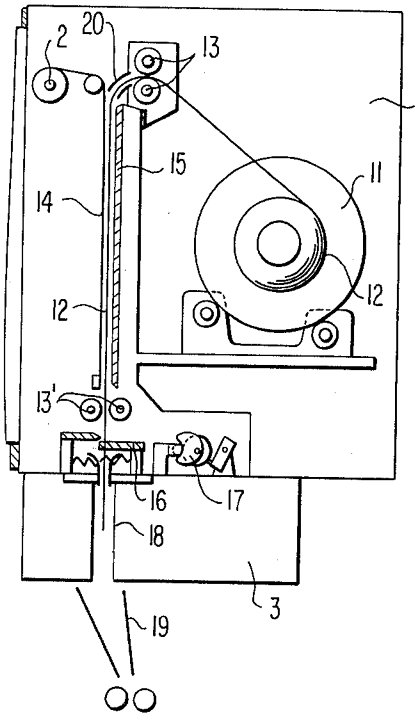

FIG. 3

PHOTO-PLATEMAKING PROCESS AND APPARATUS THEREFOR

The present apparatus may be combined with a photographing device comprising; (i) a manuscript supporting bed; (ii) a magnification controlling device for determing the position of a photographic lens according to the photographic magnification desired; (iii) a camera to photograph a manuscript on the plate substance (which has been housed in a magazine) by means of the lens; and (iv) means to convey the photographed plate substance in the form of a roll to a photoengraving device and means to cut off the conveyed part in order to automatically and continuously perform the photographing operation and the photoplatemaking operation.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a photo-platemaking process and apparatus therefor, more precisely, to a process for photo-platemaking a sheet material which consists of a hydrophilic surface part or a hydrophilic layer provided on an oleophilic support and a light-sensitive halide emulsion layer superimposed on the surface part or the layer and to apparatus for accomplishing the photo-platemaking process.

2. Description of the Prior Art

Various processes have hitherto been proposed for photoplatemaking using as a photo-sensitive layer a light-sensitive silver halide emulsion layer, which processes have, however, various defects. For example, the process described in U.S. Pat. No. 2,448,861 uses as a photosensitive substance a dichromate. In this process, the photosensitive region of the photosensitive substance is mainly in the ultra-violet region, and not only is the sensitivity of the substance low but also the preservability of a photosensitized sheet substance produced therefrom is extremely poor.

According to the processes described in Japanese Pat. Publication No. 27242/**69** or U.S. Pat. NO. 3,385,701, the printing plate consists of an oleophilic support and a hydrophilic layer applied on the surface of the support. These processes, however, involve various defects in that the adhesion of the surface of the oleophilic support and the hydrophilic layer is low, and as a result the hydrophilic layer in non-imaged parts is apt to be easily separated from the surface of the support during printing and the hydrophilic surface may be stained due to the deposition of oily inks thereon. The hydrophilic layer used in these processes consists of gelatin, colloidal silica, etc., and the hydrophilic property of the layer is not always sufficient. Therefore, oily inks gradually deposit on non-imaged parts with increased amounts of printing until the hydrophilic surface is stained. Thus, sufficient numbers of printed reproductions of high quality cannot be obtained.

Apart from the above mentioned conventional processes, British Pat. Nos. 913,591 and 998,447 describe processes for making lithographic printing plates wherein a metal plate, such as an aluminum plate having a hydrophilic surface, is used, the metal plate having activity to reduce a silver salt by a diffusion transfer process, and an oleophilic silver image is formed on the metal plate whereby the silver image forms an oleophilic part. However, aluminum is easily oxidized by air to form aluminum oxide, and thus the activity thereof as diffusion transfer nuclei is poor. Moreover, the density of the silver image deposited is apt to be low, and accordingly, it is necessary in the process of British Pat. No. 913,591 to use a specific treating solution including a chemical agent which has an affinity to the silver image deposited in order to improve the oleophilic property of the silver image deposited. In British Pat. No. 998,447 a treatment with a strong alkaline solution such as a lithium hydroxide solution is required to dissolve the aluminum oxide layer.

Silver salt diffusion transfer processes are well known in the art and in these processes imagewise unexposed silver halides of a photosensitive silver halide emulsion are imagewise converted into distributions of a soluble silver complex, and the complex is then diffused in silver depositing nuclei which convert the soluble silver complex transferred by diffusion into silver.

German Patent Laid Open for Publication Inspection (OLS) 2,048,594 describes an improved photolithographic process free from the above mentioned defects. More precisely, the process comprises the steps of, after imparting an original image exposure to a photosensitive sheet material which consists of an organic acid cellulose ester sheet having a hydrophilic surface part containing a nuclei substance for a diffusion transfer process and a light-sensitive silver halide emulsion layer applied on the hydrophilic surface, forming a reversal silver image corresponding to the original in the hydrophilic surface by means of a diffusion transfer process, and then treating with an aqeous solution containing hydrogen peroxide to remove the hydrophilic surface in places where the silver image is present to thereby expose the oleophilic surface of the organic acid cellulose ester sheet.

In this process, however, it is necessary to strongly rub the hydrophilic surface during etch-bleaching in order to expose the oleophilic surface, and due to the rubbing hydrophilic parts often remain or scratches are made. As a result it is difficult to completely expose the oleophilic surface. Moreover, when the hydrophilic surface part is thinned so that the oleophilic surface may be exposed by lightly rubbing the same, the nonimage area is apt to be stained during printing, and thin lines will be defaced.

SUMMARY OF THE INVENTION

The present invention provides an improved photoplatemaking process which is free from the defects of conventional processes and apparatus for accomplishing the improved process.

The objects of the present invention are to provide the following;

1. A process for making a printing plate which can yield a great number of print reproductions of high quality.
2. A photo-platemaking process which may be conducted by only one operator.
3. Apparatus for a photo-platemaking process for making printing plates which can yield a great number of print reproductions of high quality.
4. Apparatus for a photo-platemaking process which can be automatically conducted by only one operator in a light room.

5. An automatic processing system for a photoplatemaking process which can automatically produce a printing plate from which a number of print reproductions of high quality can be made, and which system can be operated by only one operator in a light room.

The above objects can be attained according to the process of the present invention which is characterized by the steps of, after image-wise exposing a plate consisting of a hydrophilic surface part or a hydrophilic layer provided on an oleophilic support and a silver halide emulsion layer superimposed on the hydrophilic surface part or layer, developing, washing with water, subjecting to an etch-bleaching treatment and then subjecting to an after-treatment.

Apparatus to accomplish the above purpose comprises, in combination, means to convey the plate substance being processed sequentially through a developing trough, a washing trough, an etch-bleaching trough and an after-treatment trough containing treating solutions to accomplish the indicated purpose, means for removing the silver halide emulsion layer in the washing trough and means for removing the deteriorated residues in the after-treatment trough.

In a further embodiment the apparatus described above is combined with photographing means to expose the plate substance which comprises a manuscript (original) supporting bed, means to control the desired magnification of the original for exposure of the plate substance, means in which the plate substance is exposed and means to convey and forward the exposed plate substance to the apparatus described in teh proceeding paragraph. If the plate substance is in the form of a roll, cutting means is provided to cut the plate substance to the desired length prior to developing, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of treating apparatus embodying the present invention cut along the direction of a photosensitive material for a printing plate which is being conveyed.

FIG. 2 is a side view of one embodiment of the present apparatus.

FIG. 3 is a side view illustrating the interior of a magazine box.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophilic surface part which has been provided on an oleophilic support defines a construction where at least one surface of a plastic sheet is hydrolyzed to render it hydrophilic. The hydrophilic surface part and the oleophilic layer are thus integral and the hydrophilic surface part has excellent mechanical strength, different from the hydrophilic layer as will be explained hereinunder. Accordingly, the hydrophilic surface part does not easily peel off from the oleophilic support. The total sheet thickness is usually about 80 to 300μ considering the strength of the support, the cost, and ease of handling, though greater and lesser thicknesses can be used. The thickness of the hydrophilic surface part is thinner than that of the sheet and is about 0.1 to about 30μ,preferably about 0.3 to about 10μ and most preferably 0.3–3μ.

The plastic sheets are those where the contact angle of water is more than 45° before the hydrophilic treatment, but less than 45° after the hydrophilic treatment, at normal temperature. Representatives of plastic sheets which can be treated as above are, for example, organic acid cellulose ester sheets such as a cellulose diacetate sheet, a cellulose triacetate sheet or a sheet made of a mixture of these two acetates, a cellulose acetate sheet, a cellulose propionate sheet, a cellulose butyrate sheet, a cellulose acetate butyrate sheet or the like, or an inorganic acid cellulose ester sheet such as a cellulose nitrate sheet; a polyvinyl ester sheet such as a polyethylene terephthalate sheet, a polystyrene sheet, a polyvinyl acetate sheet or the like; a polyvinyl acetal type sheet such as a polyvinyl acetal sheet, etc.

The surface part of these sheets may be made hydrophilic by hydrolyzing the same with an alkaline agent. In some cases, other treatments may be performed to impart the hydrophilic property to the surface apart. These treatments include, for example, acid hydrolysis of polyvinyl acetal, or modifying polyethylene terephthalate, polystyrene, etc. by using dichromic acid or nitric acid, or oxidizing the same by means of ozono-high frequency discharge. Processes as are typically used are taught in U.S. Pat. Nos. 2,448,861 and 2,494,053. Representative treatment baths are 50g NaOH, 400 cc ethyl alcohol, water to make 1 liter and 200 cc 10% NaOH, 400 cc ethyl alcohol, 10 cc acetone, 1000 cc water.

In the thus obtained hydrophilic surface part there are introduced silver depositing nuclei such as heavy metals, e.g., cadmium, tin, zinc, chromium, nickel, cobalt, etc., noble metals such as gold, platinum, palladium, etc., or sulfates or selenates of each of these heavy metals or noble metal salts, e.g., $SnCl_2$, $AgNO_3$, silver-citrate and the like. These materials are known to the art. See, for example, Paper presented at the conference in Liege, Apr. 15–17, 1948, by Hautot, U.S. Pat Nos. 2,698,237, 2,698,238, 2,774,667 and 2,698,245.

The silver depositing nuclei may be introduced in the hydrophilic surface part simultaneously with or after rendering the same hydrophilic.

To introduce the silver depositing nuclei the above mentioned silver depositing nuclei can be dispersed in water to form a colloidal dispersion and then contacted with the hydrophilic surface part. In this case, alcohols, ketones or chlorinated hydrocarbons can be used. These solvents have the capability particularly to swell celluloses, and so when celluloses are used it is preferable to use these solvents singly or in the form of a mixture or together with water so that the nuclei may easily be introduced into the celluloses. Accordingly, it is a most preferred embodiment of this invention to use organic acid cellulose ester sheets of the above mentioned plastic films by imparting a hydrophilic property to such ester sheets.

Representatives of the alcohols and ketones as are used include, for example, methyl alcohol, ethyl alcohol, propyl alcohol, iso-propyl alcohol, butyl alcohol, ethylene glycol, propylene glycol, polyethylene glycol, acetone, methyl ethyl ketone, methyl isobutyl ketone, etc. Particularly preferred are solvent mixtures such as water-methyl alcohol, water-ethyl alcohol-acetone, etc., since these can accelerate the hydrolysis.

The concentration of the nuclei substance can vary greatly as is known to the art, for example the concentration of NiS will generally be from as little as about 5×10^{-5} mole/l to as great as about 5×10^{-2}mole/l.

The temperature of nuclei introduction is usually from about 15 to about 60°C and usually can be up to about 10°C less than the b.p. of the solvent, with a preferred range being 20 to 50°C.

The reaction time will vary depending upon the temperature, e.g., at 50°C 5 sec.~60 sec., at 35°C 20 sec.~120 sec. and at 20°C 35 sec.~240 sec.

On the other hand, the hydrophilic layer provided on an oleophilic support means a hydrophilic colloid layer coated on a plastic sheet as described above. Examples of the hydrophilic colloids include, for example, gelatin derivatives such as gelatin, phthalated gelatin, etc., casein, alginates, polyacrylic acid, maleic acid anhydride-methyl methacrylate copolymers, vinyl derivatives (e.g. polyvinyl alcohol, polyvinyl pyrrolidone) or salts thereof such as the metal salts, e.g., Na, K, Li, NH_4 salts.

The thickness of such a layer is usually from about 0.3μ to about 10μ, preferably 0.3μ to 3μ. When the thickness is too great, it is difficult to conduct the etch-bleach.

For introducing silver depositing nuclei into the hydrophilic layer, the above mentioned silver depositing nuclei are dispersed in the hydrophilic colloid aqueous solution as heretofore described and applied onto an oleophilic support.

On the above described hydrophilic surface part or on the hydrophilic layer there is coated a silver halide emulsion layer, with a preferred thickness of the dried emulsion being from 1μ to 15μ and a preferred amount of silver being from 30μ g/cm^2 to 900μ g/cm^2.

The ratio of silver halide: binder is not important. In general, the silve halide emulsion layer is coated and dried on the hydrophilic surface part or the hydrophilic layer and the thus coated plate is then stored. When the plate is to be used, the same may be image-wise exposed. The emulsion layer is preferably non-hardened or slightly hardened, so that development may easily be performed.

The silver halide emulsion is one which has been prepared by dispersing an emulsion of a silver halide as is generally known and used in the photographic field, such as silver chloride, silver bromide, silver iodide, silver bromochloride, silver bromoiodide, silver bromoiodochloride, etc., in the above mentioned hydrophilic colloid. The silver halide emulsion can include additives as are generally used in the photographic field, such as a color sensitizer, fog preventing agent, stabilizer, hardener, surfactant, etc.

A natural or synthetic high molecular weight material layer such as an intermediate layer, protective layer or the like may be provided between the hydrophilic surface part or the hydrophilic layer and the silver halide emulsion layer, and, if desired, pigments, may be incorporated in the hydrophilic layer or intermediate layer.

The exposed silver halide emulsion layer is then developed such that the silver halide emulsion layer is contacted with the hydrophilic surface part or the hydrophilic layer. For the development, a developer for a diffusion transfer process which contains a solvent for dissolving the silver halide, such as sodium or potassium thio-sulfate, is used. The exposed silver halide emulsion layer and the hydrophilic surface part or the hydrophilic layer are dipped into the developer, more particularly, the layers are preferably dipped in the developer together with the oleophilic support from the viewpoint of ease of treatment. The developers used are well known in this photographic field, and are described in detail in "Processing Chemistry" written by Mason (The Focal Press, 1966). In the present invention, the developers used can be selected from known diffusion transfer developers without any special critical selection to the exact developer used, though typically they are developers having hydroxy groups and amino group at the ortho or para-position, e.g., dihydroxybenzenes such as hydroquinone, chlorohydroquinone, bromohydroquinone, toluhydroquinone, t-butylhydroquinone, p-methyl phenolsulfate, triaminophenol, pyrogallol, alkoxy substituted hydroquinones, the amino/phenol group compounds often being used as a salt, e.g., of HCl, H_2SO_4, 3-pyrazolidones, e.g., 1-phenyl-3-pyrazolidone, e.g., 4-amino-5,6-dihydroxy-dimethyl pyrimizine, etc.

The developers are used in their art recognized amounts, e.g., 5~35 g/l for the dihydroxybenzenes.

The silver halide dissolving agents can be selected from those known to the art, e.g., NaSCN, KSCN and $Na_2S_2O_3$ and are used in an amount as in common in this art, e.g., 4 g/l to 30 g/l.

In the process of the present invention when a non-hardened or slightly hardened emulsion is used for the purpose of performing the treatment speedily and in a stable manner, the development must be conducted at a temperature such that the emulsion layer is not melted. This temperature is, in general, lower than 30°C. On the other hand, the lowest limit of the temperature is preferably higher than 0°C for purposes of preventing the developing speed from being too slow. The most generally used practical developing temperature are 10°~35°C, preferably 15°~25°C. The developing time can easily be determined by those skilled in the art according to the kind of developer, the developing temperature and other conditions, and is usually from 10 sec to 50 sec., preferably 20~40 sec.

After a positive silver image is formed on the silver depositing nuclei by diffusion transfer development, the silver halide emulsion layer becomes unnecessary, and so this layer is removed from the hydrophilic surface part or the hydriphilic layer by washing with water. In this treatment, when the above mentioned protective layer or intermediate layer is present it is removed together with the emulsion layer.

The temperature for the washing with water is selected to make the removal of the emulsion layer from the hydrophilic surface part or the hydrophilic layer easy, and in general is at least 35°C, with a minimum of 40°C providing better results. A preferred operational range is 45°~55°C. The hydrophilic surface part is peeled from the oleophilic support only with difficulty, as compared with the hydrophilic layer, and so when the hydrophilic surface part is used the emulsion layer can be peeled therefrom by means of a roller or the like without injuring the hydrophilic surface part.

In the water used for washing there may optionally be incorporated accelerating agents such as a protein decomposing enzyme, thiocyanate, urea, etc., which render the washing with water easier to accomplish.

The hydrophilic surface part or the hydrophilic layer which has been washed with water is then subjected to an etchbleaching treatment. The etch-bleaching treatment is a means to expose the oleophilic surface corresponding to the silver image part. According to this treatment, the hydrophilic surface part or the hydrophilic layer corresponding to the image part is deteriorated. The term deterioration means the phonomenon that the hydrophilic surface part or the hydrophilic layer containing a silver image becomes easily removed from the plastic sheet by means of the etch-bleaching treatment, as compared with portions that do not contain a silver image. Nonetheless, the sheet thus treated still has faults for use as a printing plate.

The etch-bleaching solution used includes an oxidizing agent as is used in common photobleaching solutions, such as sodium ferrihexacyanate di-chromate, hydrogen peroxide, etc. In particular, peroxodisulfate has good stability in solution, and so peroxosulfate or peroxodisulfate are a preferred oxidizing agents. These may be used singly or in the form of a mixture thereof, and a most effective amount is 0.35°~30% by weight of the treating solution.

In order to accelerate the etching action, at least one of a cupric salt, an acid or a substance which reacts with silver to form a complex of low solubility can be present in the etching solution. Examples of useful cupric salts include water soluble cupric salts such as cupric chloride, cupric bromide, cupric nitrate, cupric sulfate, cupric citrate, etc. Cupric halides are preferred. Examples of useful acids include organic acids such as acetic acid, citric acid, tartaric acid, phthalic acid, maleic acid, benzene sulfonic acid, etc., and inorganic acids such as hydrochloric acid, nitric acid, sulfuric acid, etc.

Examples of substances which react with silver to form a compound of low solubility include halides, tartrates, carbonates, chromates or formates. In particular, halides are preferred, e.g., NaBr, KCl, KBr, LiBr, NH_4Br, NaI, KI, $SrBr_2$, etc.

Accelerators and/or such materials which react with silver are described in, for example, U.S. Pat. No. 3,385,701, British Pat. No. 587,957 and OLS. 2,048,594.

These accelerating agents may be used singly or in the form of a combination thereof. The amount of accelerating agent is usually 0.05~50% by weight of the treating solution. (Some compounds have a solubility of lower than 50%, but an amount thereof more than 0.05% will suffice.)

When peroxodisulfate is used together with at least one of the above mentioned etching accelerating agents (cupric salt, acid or substance which reacts with silver to form a complex of a low solubility), the amount of the peroxodisulfate is, calculated in terms of ammonium peroxo-disulfate, 0.0125~30% by weight of the treating solution.

The preferred amount of the peroxodifulfate is, calculated in terms of ammonium peroxo-disulfate, 0.1–20% by weight, considering the stability of the etching solution with the passage of time and the stability of the photosensitive material. Using this solution the parts of the hydrophilic layer corresponding to the silver image are etched at 5°–40°C within 30 seconds and are deteriorated.

The etch-bleaching temperature is usually 5°–45°C, preferably 10° to 40°C considering the stability of the etching-bleaching solution with the passage of time and the reaction speed. The etch-bleaching time can vary greatly but from 10 to 60 sec. will suffice for most elements processed.

The preferred etch-bleaching solutions contain an oxidizing agent, an acid, and a material which forms an insoluble compound with silver, e.g., see British Pat. No. 587,957, U.S. Pat. No. 833,274, U.S. Pat. No. 3,385,701 and OLS 2,048594.

The surface of the sheet material treated by etching is lightly rubber whereby the hydrophilic surface part corresponding to the silver image is easily removed and thus the oleophilic surface of the sheet is exposed. On the other hand, the hydrophilic surface part free of silver image remains as such. The thus manufactured printing plate can be used as is as a direct or offset printing plate according to conventional processes. In addition, the plate can subjected to an after-treatment to obtain a desired planographic printing plate having better properties.

The term after-treatment defines a treatment whereby the residues which have been deteriorated by the aforementioned etchingbleaching treatment are rendered fragile and, for example, comprise treating the hydrophilic surface part or the hydrophilic layer which has been subjected to etching-bleaching with a solution of a chlorine-oxygen acid such as chlorous acid, hypochlorous acid or perchloric acid or a salt of such an acid, a water soluble thiocyanate, a dyestuff which is physical adsorbed to the hydrophilic surface part of the hydrophilic layer and having (an) anion substituent(s), or a mixture thereof.

The "fragile" residues which result have been deteriorated by the etching-bleaching treatment and they may be completely removed by this after-treatment, or, in certain cases, may be easily removed merely by lightly wiping the surface by means of a sponge, cotton, wool, etc., without injuring the hydrophilic surface part or the hydrophilic layer in the non-image part, whereby operational efficiency is extremely improved. The printing plate finally obtained yields print reproductions having extremely high sharpness and resolving power.

When the hydrophilic surface part embodiment is used a particularly superior effect can be attained by the after-treatment.

In the non-dyestuff emobdiments of the after treatment the temperature is generally from about 5° to about 80°C. preferably 10° to 40°C., with the concentration of active ingredient generally being from 0.1~30%, preferably 0.2~5%, by weight, based on one liter of after treatment both, though in the case of KSCN, the concentration is advisably 0.1 to 20%, and in the case of NaClO, it is acceptable to use 2~30 mols % of NaClO containing 10% effective Cl per liter.

As examples of the dyestuffs mentioned above, there are direct dyes, basic dyes, naphthol dyes (coupling components of azoic dyes), acid dyes, etc. as described in the Japanese book entitled "Handbook for Dyes" (published by Maurzen Publishing Co. in 1970), pages 83 and 245–246. Examples of anionic substituents as are used include the sulfonic group, sulfinic group, $-CO_2^{2-}$ group, $-CS_2^{2-}$ group, carboxyl group, etc., in the form of an acid and/or a salt, e.g., an Na, K or NH_4 salt.

The direct dyes contain one or more anionic substituents such as sulfonic groups, etc. In the after-treatment of the present invention, any type of the direct dye may be used, and particularly preferred dyes are for example: C.I. Direct Yellow 11, C.I. Direct Yellow 12, C.I. Direct Yellow 26, C.I. Direct Yellow 39, C.I. Direct Yellow 44, C.I. Direct Yellow 50, C.I. Direct Orange 6, C.I. Direct Orange 8, C.I. Direct Orange 10, C.I. Direct Orange 26, C.I. Direct Orange 39, C.I. Direct Orange 49, C.I. Direct Orange 51, C.I. Direct Red 1, C.I. Direct Red 2, C.I. Direct Red 4, C.I. Direct Red 9, C.I. Direct Red. 13, C.I. Direct Red 20, C.I. Direct Red

23, C.I. Direct Red 28, C.I. Direct Red 31, C.I. Direct Red 37, C.I. Direct Red 62, C.I. Direct Red 79, C.I. Direct Red 80, C.I. Direct Red 81, C.I. Direct Red 83, C.I. Direct Red 89, C.I. Direct Red 224, C.I. Direct Red 225, C.I. Direct Red 226, C.I. Direct Red 229, C.I. Direct Red 230, C.I. Direct Violet 47, C.I. Direct Blue 1, C.I. Direct Blue 71, C.I. Direct Blue 78, C.I. Direct Blue 86, C.I. Direct Blue 98, C.I. Direct Blue 106, etc.

Many basic dyes contain cationic groups, for example, Mehtylene Blue, Malachite Green Crystal Violet, Victoria Blue, etc., and do not contain any anionic substituent. Such basic dyes cannot be used in the present invention. On the other hand, basic dyes containing anionic substituents, for example, C.I. Basic Violet 10 (Rhodamine B), etc. can be used in the present invention whereby the same effect as in the case of the above mentioned direct dyes can be attained.

The naphthol dyes which can be used are naphthol series substances which are coupling components of azoic dyes, for example, 2-hydroxy-naphthalene-3-carbonyl-anilide-4′-sodium sulfonate, etc. In other words, the naphthol dyes are substances that have as a base skeleton the 2-hydroxy-3-naphtho-anilide group. Accordingly, compounds that contain additional substituent(s) and/or condensed ring(s) in the naphthalene nuclei and/or benzene nuclei of the 2-hydroxy-3-naphthoic acid anilide are included in the class of naphthol dyes which can be used in the present invention, e.g., alkyl, alkoxy, phenyl, anthraquinone, etc., substituted materials.

Acid dyes containing anionic substituents are, in general, inferior to the direct dyes with respect to physical adsorbability to plastics, especially to hydrophilic cellulose at normal temperature. However, when the temperature of the aqueous solution of the dyes is elevated, e.g., to 50° to 90°C, the physical adsorbability may be improved and thus such dyes can be used in the present invention at such elevated temperatures. Representatives of such acid dyes are, for example C.I. Acid Yellow 19, C.I. Acid Yellow 99, etc.

Most of acid dyes containing anionic substituents are similar to those mentioned above, but some acid dyes can provide the same effect as the direct dyes even at normal temperature. Although this class of dyes is very limited, such acid dyes are effective in the present invention, and include, for example, C.I. Acid Blue 158, C.I. Acid Red 186, C.I. Acid Red 265, etc.

The above mentioned direct dyes, basic dyes, naphthol dyes and acid dyes can be used singly or as mixtures of two or more thereof.

The concentration of the solution of these dyes can vary, depending upon the kind of the dyes used, the properties of the layer to be etched such as the degree of hardness, kind, thickness, etc. of the layer, as well as the temperature of the solution of the dyes. While the concentration will thus vary depending on a number of factors, in general the dye is present in an amount of greater than 0.01% by weight of the solution. The dyes can also be used in the form of a supersaturated solution at a certain temperature and in a certain solution constitution. Preferably, the solution contains about 0.5–5% by weight of the dyes.

The pH value of the solution of the dyes may be acidic, neutral or alkaline state, but in particular the alkaline state is preferred, with a neutral to weakly alkaline state of pH 7–11 being most preferred. Accordingly, usually an appropriate adjustment of the pH of the dye solution will be performed, if necessary. For this adjustment, an alkali such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, etc., or an acid such as acetic acid, sulfuric acid, hydrochloric acid, nitric acid, etc. is used.

The temperature of the solution of the dyes to be used is, in general, in the range of 2°–90°C, and more preferably 10°–50°C. The treating period varies, depending upon the properties of the layer to be etched, the constitution of the solution of the dyes, etc. In general, the treating period is in the range of from for 5 seconds to for 5 minutes.

To the solution of the dyes which contain at least one anionic substituent and which physically adsorb onto the hydrophilic surface part or the hydrophilic layer of the present invention, additional organic solvents which are miscible with water may be added as auxiliary solvents, for example, a solvent containing a hydroxyl group(s) such as methanol, ethanol, ethylene glycol, isopropyl alcohol, etc., a ketone series solvent such as acetone, methyl-ethyl detone, etc., or an ether series solvent such as ethylene glycol monomethyl ether, ethylene glycol diethyl ether, etc. Generally from 2–60% organic solvent based on solution weight can be used, with organic solvents in a small amount (2–20%) in water being more preferred.

The use of such an after-treating solution containing dyes imparts an especially excellent effect to cellulose having a hydrophilic surface part or to cellulose having a hydrophilic layer.

The treatment by the use of such treating solution is, in general, performed after the treatment by the use of the etching-bleaching solution. Water washing may be performed between these two treatments.

According to the above mentioned after-treatment, various advantageous effects as mentioned above may be attained, and thus, a printing plate of high quality may be obtained from which a number of print reproductions having a high sharpness can be produced.

An additional effect is as follows: When the above mentioned dyes other than the naphthol dyes are used the dyes are adsorbed only on the non-image parts which are not etched, and so various kinds of colored reversal images can be obtained according to the kind of the dye used. Therefore, when the after-treatment of the present invention has been performed during processing in a photo-platemaking process, the question of whether or not the etching process was complete or whether or not the reproduction of a namuscript is sufficient can usually be confirmed without inking the obtained printing plate. As a result, the operational efficiency of the present process is improved.

When a printing plate obtained by the present invention is brought to a heat projector before being inked eyestrain does not occur since the difference between the part colored with dyes and that not colored is extremely vivid.

It should be noted that generally speaking the development, water washing, etch-bleaching and aftertreatment can be completed within 15–45 seconds, and with the use of the apparatus described below extremely rapid and efficient processing could be conducted, e.g., in from 1 minute to 3 minutes.

The apparatus for the photo-platemaking process of the present invention will be now explained with reference to the drawings attached hereto.

With reference to the FIG. **1**, **10** is the overall apparatus assembly. Each of treating troughs **22A–22D** is filled with treating solution to be used in the present photo-platemaking process. Apparatus **10** has almost the same construction as a conventional automatic treating machine which is used for DP work (photographic development and printing), etc., with the exception of sponge rollers **27** and pressing plates **28** placed in the fourth through **22D**, which will be explained hereinunder.

A brief explanation of apparatus **10** is as follows: the treating throughs **22A** to **22D** consist of troughs of a developing bath **22A**, a water wahsing bath **22B**, an etching-bleaching bath **22C** and an after-treating bath **22D**. The conveyance of the substance to be treated is performed by means of roller twins **24** and guide plates **23** and **25**, that is, the conveying means is a roller conveyance.

Heaters **26** and devices for cooling water circulation **36** are optionally provided for the purposes of controlling the liquid temperature. A taking-up lid **32** is provided for the purpose of taking up the plate treated in the first trough **22A** and the second trough **22B**, and in general lid **32** is shut to exclude light from the interior of the treating troughs. The developer may be checked according to the degree of development of the developed plate.

A detailed explanation will now be given, with reference to apparatus **10** shown in the FIG. **1** with respect to how to treat and process the printing plate of the present invention consisting of a hydrophilic surface part or a hydrophilic layer which contains silver depositing nuclei for diffusion transfer and which has been provided on an oleophilic support, with a silver halide emulsion layer superimposed on the surface part or the layer.

The plate to be used for printing which has been photographed by means of a camera for photoengraving or the like is brought into the interior of apparatus **10** by means of a guide plate **19**, and is then successively conveyed to the first trough, the second trough, the third trough and the fourth trough in this order, finally forming a printing plate.

The first trough **22A** is a developing bath. This trough is filled with a developer consisting of the components described above at 0°–30°C. The plate is conveyed into the developing bath whereby the exposed silver halide emulsion layer on the plate is subjected to a diffusion transfer development. When the plate has reached the outlet of the first trough **22A**, a positive silver image is formed in the hydrophilic surface part or the hydrophilic layer of the plate.

The second trough **22B** is a water washing bath. The plate passed through the first trough is forwarded into the water washing bath **22B** along the guide plate **25** where the silver halide emulsion layer is removed. When auxiliary layers such as the protective layer, intermediate layer or the like are present, these layers are also removed at the same time. The water for washing is warm water having a temperature of higher than 40°C. For the removal of the emulsion layer, it is sufficient to provide a rotary removing means or the like in this trough which does not impart damage such as scratches or the like to the plate substance. In particular, it is especially effective to provide pairs of rollers in the second trough to make the linear velocity of the rotary device different from the conveying speed of the plate whereby a higher effect is attained.

In FIG. **1** one embodiment is shown of a removing device consisting of sponge rollers **27** and pressing plate **28**. The sponge rollers **27** may also be placed so as to face each other. The removing means is not limited to sponge rollers. The rotary removing device can optionally be provided at the outlet of the water washing bath **22B**.

In the plate sent out from the second trough **22B**, the silver halide emulsion layer is removed off and the hydrophilic surface part or the hydrophilic layer which contains a silver image is exposed.

The third trough **22C** is an etch-bleaching bath. The plate forwarded from the second trough **22B** to the third trough is subjected to etch-bleaching treatment in the third trough. The various conditions such as the composition of the liquid supplied to the third trough, the temperature of the liquid and the like may be selected from a wide range as in the case of the treatments in the first trough **22A** and second trough **22B**. By the etchbleaching treatment, the hydrophilic surface part or the hydrophilic layer corresponding to the image part is deteriorated. In this stage, the plate can be used as a printing plate, but will usually not yield sufficient print reproductions. The plates thus subjected to the etching-bleaching treatment are further conveyed to the fourth trough **22D**.

The fourth trough **22D** is an after-treating bath wherein the plate which has been subjected to etch-bleaching treatment is after-treated. The after-treatment means, as mentioned above, is to make the hydrophilic surface part or the hydrophilic layer which has been deteriorated by means of the etch-bleaching solution brittle. Accordingly, the plate sent out from the fourth trough **22D** may be used as a printing plate as such, or by merely rubbing the surface of the plate by means of an elastic substance such as sponge, fabric or the like.

In order to omit the treatment for rubbing the surface of the plate by means of the elastic substance after the aftertreatment in the fourth trough **22D**, or to make the treatment, easier, a removing means may be provided in the fourth trough **22D**, i.e., which provides the same effect as the optional removing device provided in the second trough **22B** for the purpose of removing the silver halide emulsion layer. More precisely, the hydrophilic surface part or the hydrophilic layer which has been deteriorated in the third trough **22C** and any remaining silver halide emulsion layer are removed by means of sponge rollers **27** and a pressing plate **28**. Any substance may be used for this removing means which has a removing effect and which does not damage the surface of the plate.

The plate on which the treatment in the treating trough **22D** has been completed is optionally put on a receiving plate **31** to be an original plate for printing via a drying device provided at the end part of the apparatus **10**.

FIG. **2** shows an apparatus for a photo-platemaking process which comprises the apparatus shown in the FIG. **1** with a camera device combined therewith. More precisely, this apparatus is composed of a manuscript supporting bed **8**, a photomagnification controlling device for changing the relative position of a mirror **4** and a lens **5**, a device for conveying a plate substance to the photoengraving device and for cutting off the conveyed part, the plate substance having been photographed in the interior of a camera device, e.g., by photographing the image of the manuscript on the plate substance in the form of a roll which has been housed in the magazine box **1**, by means of the mirror **4** and the lens **5**, and photo-engraving apparatus **10** as shown in the FIG. **1**.

The manuscript supporting bed **8** is movable parallel to the surface of the floor to change the relative position with the lens series device in order to obtain any desired photograph such as magnified, equivalent or reduced by means of the photomagnification controlling device.

For photography, the manuscript is fixed on the manuscript supporting bed **8** by means of a glass plate so as to keep the manuscript even.

A light projector **7** is movable so as to evenly light the surface of the manuscript. When the intensity of illumination on the manuscript bed is increased by using a plurality of light sources, the luminance of the respective light source may often vary individually with the lapse of time. In order to avoid such individual variation of the illumination, the relative position and angle of the light source and the manuscript supporting bed are adjustable.

It is necessary that a positive image of the manuscript be photographed on the printing plate substance by means of the camera device **9**. For this purpose, the mirror **4**, a prism or the like, is incorporated in the optical system. The lens **5** and a shutter iris are similar to the lens system of a photoengraving camera. Elements **2** and **3** are explained in detail in the discussion regarding FIG. **3**.

FIG. **3** illustrates the interior of magazine box **1**. The leading end part of a plate substance **12** which has been rolled up in the form of a roll in a spool **11** is conveyed via roller twins **13** and guide plates **20** and the plate substance is kept in a flat state on a plate supporting plate **15**, that is, in the position where the plate substance is photographed, by means of roller twins **13** and **13'**. The photosensitive material **12** may be positioned by applying suction to the material **12** under vacuum from the back surface of the light-sensitive surface thereof or by pressing the whole surface of the material **12** on the camera back **15** by means of a plate which is transparent to light.

The plate substance **12** is conveyed downward by means of the rollers **13** and after a plate having a determined size has been conveyed to the desired position by the action of a cam **17** which is operated by a timer (not shown) the plate **12** is cut in the form of a sheet by means of a cutter **16** which is set to cooperate with the cam **17**. The thus cut sheet is conveyed to the photo-engraving apparatus via a slit **18** in a flexible skirt **3**. **19** is a guide to forward the cut plate substance to the processor.

A light-excluding curtain **14** is slidable so as to cover the front surface of the plate **15** by operating a handle **2** at the outside of the magazine box **1**, whereby the plate substance **12** may economically be utilized according to the size of the manuscript.

As the plate substance, a sheet-type substance may, of course, be used.

The process of photographing and conveying the plate substance to the photoengraving apparatus will now be explained with reference to the combination apparatus of the camera device **9** and the photo-platemaking apparatus **10**.

A manuscript evenly set on the manuscript supporting bed **8** is kept at the necessary photomagnification by appropriately controlling the positions of the supporting bed **8** and the lens **5** according to the desired photomagnification. Next, the manuscript is photographed on the plate substance which has been prepared on the plate supporting plate **15** by means of the lens **5**. After the completion of the photographing, the plate substance is conveyed in the necessary length by the roller twins **13** and **13'** and is cut by the cutter **16**. The cut plate substance sheet is conveyed to the photo-engraving apparatus via slit **18** in the skirt **3**. On the other hand, the remaining plate substance roller **12** is kept on the plate supporting plate **15** and is prepared for the next photographing.

The treatments to be performed thereafter in the respective treating troughs of the photo-platemaking apparatus have already been explained hereinbefore in detail.

According to the photo-platemaking apparatus of the present invention continuous processing from the photographing of a manuscript to the photo-platemaking of printing plate may automatically be performed even in a light room by operating a control box (not shown) for the apparatus.

As will be apparent from the above explanation, the process and the apparatus of the present invention have the following merits.

1. Printing plates may be produced having good reproductivity and a high printing resistance, which plates may therefore reproduce print reproductions having an excellent image quality. This effect becomes particularly noticeable after the after-treatment has been performed.

2. Printing plates may be produced which can be visually checked by the coloration thereof without inking.

3. The silver halide emulsion layer after being developed may be completely removed by means of a pair of twin rollers in the water washing trough for the removal of the silver halide emulsion layer without any formation of foam in the washing water. This effect is favorable for the treatments after washing.

4. Printing plates may be produced speedily and simply by one operator.

5. Printing plates may be produced automatically and speedily in a light room by one operator.

The above mentioned merits are particularly noticeable when the process of the present invention is combined with the apparatus of the present invention, and more preferably, it is advantageous to use a hydrophilic surface part for obtaining practical effects. Sufficient effects may, of course, be obtained by means of the other embodiments.

The present invention will now be explained in more detail by the following examples which, however, do not limit the scope of the present invention.

EXAMPLE 1

Solution A		
Glycerin	50	ml
Methyl alcohol	300	ml
Sodium sulfate (9 H_2O)	1.2	g
Sodium carbonate (1 H_2O)	0.5	g
Water	10	ml
Solution B		
Cadmium acetate (2 H_2O)	13.3	g
Water	10	ml

Solution B was added to Solution A over 5 minutes (while being stirred) to form Solution C wherein cadmium sulfate was dispersed. 100 g of the Solution C were mixed with Solution D of the following composition to prepare Solution E.

Solution D	
Water	800 ml
Sodium hydroxide	200 ml
Ethyl alcohol	1200 ml

A cellulose triacetate sheet having a thickness of 135μ was dipped in Solution E for 40 seconds at 40°C and was washed with warm water and dried, whereby an image receiving sheet for diffusion transfer printing was formed.

A silver bromoiodide emulsion (5 mol % of silver iodide) containing 1.2 mols of silver per 1 kg of emulsion which was ortho-sensitized by means of a sensitizing dye was applied in a thickness of 5μ to the sheet.

The silver halide emulsion layer was image-wise exposed and then developed using a developer of the following constitution for 30 seconds at 20°C.

Developer composition	
Water	750 ml
p-Methyl-aminophenol sulfate	5 g
Sodium sulfite anhydride	65 g
Sodium thiosulfate anhydride	10 g
Hydroquinone	15 g
Sodium hydroxide	20 g
Water to make 1000 ml	

After development, the sheet was dipped in warm water at 50°C while keeping the silver halide emulsion layer in contact with the hydrophilic surface part, whereby the silver halide emulsion layer was removed from the hydrophilic surface part. At this time a positive silver image deposited by the development is present in the hydrophilic surface layer.

The hydrophilic surface part was then dipped in an etch-bleaching solution of the following constitution for 25 seconds at 15°C.

Etch-bleaching solution composition	
Cupric chloride (2 H_2O)	10 g
Acetic acid	10 g
Peroxoammonium disulfate	120 g
Water to make 1500 ml	

In this stage the hydrophilic surface part containing the silver image was deteriorated. In order to completely remove the deteriorated part, however, the surface had to be strongly rubbed by means of cotton, wool or another soft fabric. The cellulose triacetate sheet having a hydrophilic surface part and an oleophilic part which has been obtained at this stage may be used as a printing plate as such.

The cellulose tri-acetate sheet which was subjected to the etch-bleaching treatment was further dipped in an aftertreating solution of the following constitution at 40°C for 20 seconds.

After-treating solution composition	
C.I. Direct Blue 76	32 g
Water	950 ml

The deteriorated residue in the silver image part was removed very easily from the after-treated hydrophilic surface part. The thus obtained printing plate was colored in the non-image parts (that is, the part not containing any silver image), and thus it was confirmed that the etching was accurately completed.

This printing plate was set on an offset printing machine for printing and 5,000 print reproductions were obtained. During printing, the hydrophilic property of the non-image part of the printing plate was not damaged and scratches did not occur on the surface of the printing plate, and so the image lines of the produced prints were very sharp. This means the printing resistance of the printing plate obtained according to the above mentioned process is superior to that of a printing plate which was obtained merely by the etch-bleaching treatment or without the after-treatment.

EXAMPLE 2

A cellulose diacetate sheet (thickness 155μ) was dipped in the following Solution D for 45 seconds at 40°C, whereby the surface part of the sheet was hydrolyzed to become hydrophilic and, at the same time, nickel sulfate was introduced in the said surface part. An image receiving sheet for diffusion transfer was thus obtained.

Solution A		
Glycerin	100	g
Ammonium sulfate (aqueous solution wherein the sulfur content is 14.3%)	40	ml
Solution B		
Glycerin	180	g
Nickel nitrate (6 H_2O)	0.5	g

Solution A and Solution B were mixed together at 30°C over 5 minutes (while being stirred) to form Solution C. 250 g of Solution C were mixed with a solution consisting of 3,000 g of methyl alcohol, 2,000 g of water and 500 g of sodium hydroxide to form Solution D.

To the above mentioned image receiving sheet there was applied, at a thickness of 3μ, an emulsion layer of silver bromochloride (silver chloride 75 mol %) which contained 1 mol of silver per 1 kg of emulsion and which was subjected to gold sensitization and which had been ortho-sensitized by means of a sensitizing dye. This silver halide emulsion layer was image-wise exposed and developed for 25 seconds at 25°C using the following developer.

Developer composition		
Sodium sulfite anhydride	100	g
Hydroquinone	20	g
1-Phenyl pyrazolidone	1.0	g
Sodium thio-sulfate	10	g
Potassium bromide	2.5	g
Potassium hydroxide	18	g
Water to make 1000 ml		

After development, the sheet was dipped in warm water at 55°C, the silver halide emulsion layer and the hydrophilic surface part being kept in contact, whereby the silver halide emulsion layer was removed from the hydrophilic surface part.

Next, the hydrophilic surface part was dipped in an etch-bleaching solution consisting of the following components for 25 seconds at 25°C.

Etch-bleaching solution composition	
Cupric sulfate (5 H_2O)	20 g
Citric acid	90 g
Potassium bromide	5 g
Peroxoammonium disulfate	65 g
Water to make 1000 ml	

At this stage the hydrophilic surface part containing a silver image was deteriorated. In order to completely remove the deteriorated part, however, the surface had to be strongly rubbed by means of a fabric, sponge or cotton. The cellulose diacetate sheet having a hydrophilic surface part and an oleophilic part which has been obtained in this stage can, however, be used as a printing plate as such.

The above mentioned cellulose diacetate sheet which had been subjected to etch-bleaching treatment was further dipped in an after-treating solution consisting of the following components at 25°C for 30 seconds.

After-treating solution composition	
C.I. Direct Orange 39	20 g
Sodium carbonate	1 g
Water	1000 ml

The deteriorated residues in the silver image part were easily removed from the hydrophilic surface part thus after-treated merely by lightly rubbing the surface with a soft sponge.

The non-image part of the thus obtained printing plate was colored and checking of the plate was easy. The plate was subjected to offset printing and 6000 sharp reproductions were obtained.

EXAMPLE 3

Silver was coated by vacuum evaporation coating a cellulose triacetate film, and then the film was dissolved in methylene chloride. A polyethylene terephthalate film (thickness 100μ) coated with a gelatin subbing layer was coated with the solution resulting from the dissolution at a thickness of about 4μ.

This sheet was hydrolyzed with a solution consisting of the following components to form a hydrophilic surface part about 1.2μ thick containing silver depositing nuclei.

Hydrolyzing solution composition	
Lithium hydroxide	35 g
Ethylene glycol	100 g
Methyl alcohol	550 g
Water	400 ml

Onto the hydrophilic surface layer a silver chloride emulsion layer (ratio of silver to gelatin 1:2) was coated at a thickness of about 4μ, and then the emulsion layer was image-wise exposed.

This plate substance was then dipped in a developer of the following constitution for 30 seconds at 20°C.

Developer composition	
Sodium sulfite anhydride	75 g
Hydroquinone	18 g
Sodium thio-sulfate anhydride	10 g
Potassium bromide	2 g
Potassium hydroxide	19 g
Water to make 1000 ml	

After development, the plate was washed with water at 40°C for 30 seconds while the layers were kept in contact. By the washing the silver halide emulsion layer was removed and a positive silver image was deposited on the hydrophilic surface part.

This plate was treated with an etch-bleaching solution of the following constitution for 30 seconds at 25°C.

Etch-bleaching solution composition	
Cupric bromide	6 g
Phosphoric acid	6 ml
Peroxopotassium disulfate	140 g
Water to make 1000 ml	

At this stage, the hydrophilic surface part containing the silver image was deteriorated. In order to completely remove the deteriorated part, however, the surface had to be strongly rubbed by means of a fabric or sponge.

The hydrophilic layer subjected to the etch-bleaching treatment was then dipped in an after-treating solution of the following composition at 45°C for 14 seconds, whereby a printing plate having high printing resistance and able to reproduce a printed image of good sharpness was obtained.

After-treating solution composition	
C.I. Direct Blue 71	30 g
Water	1000 ml

This printing plate was used for offset printing and 8000 print reproductions of high quality were obtained.

EXAMPLE 4

A cellulose acetate butyrate sheet having a thickness of 38μ and a polyethylene terephthalate sheet 100μ thick were laminated and hydrolyzed for 6 minutes at 20°C using the following solution:

Water	500 g
Methyl alcohol	500 g
Sodium hydroxide	70 g

The sheet whose surface part was hydrolyzed was neutralized by means of a 5% acetic acid aqueous solution and was then washed with water and dried. This sheet was dipped in a 0.03% chloroaurate-methyl alcohol solution at 35°C for 30 seconds and then dried. It is preferred to use ultra-violet drying, though even without such if the sheet is left as such at normal temperature for 1 day sufficient amounts of diffusion transfer nuclei are deposited in the hydrolyzed surface part of the cellulose triacetate sheet.

A silver bromochloride emulsion layer (silver chloride 70 mol %) containing 1 mol of silver per 1 kg of emulsion was coated on the sheet at a thickness of 3 μ, and then the layer was exposed image-wise and developed for 40 seconds at 25°C using a developer of the following composition:

Water	750 ml
p-Methyl-aminophenol sulfate	5 g
Sodium sulfite anhydride	65 g
Hydroquinone	15 g
Potassium thiocyanate	25 g
Sodium hydroxide	20 g
Water to make 1000 ml	

After the silver halide emulsion layer was removed in warm water at 50°C, a positive silver image was obtained.

The plate was next immersed in an etching-bleaching solution of the following composition at 25°C for 30 seconds.

Cupric bromide (2 H_2O)	12 g
Glacial acetic acid	50 ml
35% Hydrogen peroxide solution	100 ml
Water	900 ml

At this stage the residues which had been deteriorated by means of the etch-bleaching solution can be removed only by strongly rubbing the surface of the plate. After the plate was treated with the after-treating solution having the following components, the deteriorated residues were removed quite easily and scratches did not occur on the non-image part. Thus a printing plate whose image part was etched sharply was obtained. The thus obtained plate was used for offset printing and more than 15,000 print reproductions were obtained.

After-treating solution composition	
2-Hydroxy-naphthalene-3-carboxyaniline-4'-sodium sulfonate	30 g
Water to make 1000 ml	

EXAMPLE 5

A polystyrene sheet (thickness **120 μ**) was dipped in concentrated sulfuric acid for 10 seconds at 50°C to sulfonate the surface part thereof, washed with water and then dipped in a **1**N sodium hydroxide solution to neutralize the acid. The sheet was again washed with water and dried.

Next, this sheet was dipped in a dispersion of colloidal nickel sulfide which was formed in 80 g of ethylene glycol monobutyl ether, 15 g of methyl alcohol and 5 g of water (colloidal nickel sulfide concentration = 3×10^{-3} mols/l), for **60** seconds at 30°C to introduce nickel sulfate into the surface part, whereby a sheet having a transparent hydrophilic surface part was obtained.

A silver chloride emulsion layer wherein the ratio of silver to gelatin was 1:2 was coated on this surface, and then the layer was exposed and washed with water as in Example 3. A black positive silver image was thus obtained. This was treated with the etching-bleaching solution of Example 1 for 25 seconds at 30°C and then further treated with the following solution for 30 seconds at 25°C to obtain a printing plate.

C.I. Direct Red. 31	25 g
Water to make 1000 ml	

This printing plate was used for offset printing, and sharp print reproductions were obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A photo-platemaking process for making printing plates which comprises the steps of:

1. image-wise exposing a plate substance for making a photoplate, which plate substance consists of a hydrophilic surface part or a hydrophilic layer provided on an oleophilic support and containing therein silver depositing nuclei for a diffusion transfer process and a silver halide emulsion layer superimposed thereon, and then developing the exposed plate substance to form a positive silver image on the hydrophilic surface part or on the hydrophilic layer,
2. washing the developed plate substance with water to remove the silver halide emulsion layer,
3. subjecting the hydrophilic surface part or the hydrophilic layer to an etch-bleaching treatment to thereby deteriorate the hydrophilic surface part which corresponds to the silver image,
4. subjecting the product of step (3) to an after treatment which is conducted with either a 0.1 to 20% by weight solution of KSCN, based on one liter of after treatment, at a temperature from about 5° to about 80°C, or with a solution of a dyestuff which is a direct dye, basic dye, naphthol dye, or acid with an anionic substituent of a sulfonic group, sulfinic group, —CO_2^{2}— group, —CS_2^{2}— group or carboxyl group, and whereby the dyestuff is physically adsorbed to the hydrophilic surface part or hydrophilic layer, whereby the residues of any etched-bleached portions are made brittle and fragile, and
5. removing the residues.

2. The process of claim **1** where the hydrophilic materials have a contact angle with water less than 45°C and the oleophilic support has a contact angle with water greater than 45°, at normal temperature.

3. The process of claim **2** where the oleophilic support is a cellulose ester.

4. The process of claim **1** where the total thickness of the oleophilic support and the hydrophilic surface part or layer is from about 80 to about 300μ.

5. The process of claim **4** where the hydrophilic surface part or layer is about 0.1 to about 30 μ thick.

6. The process of claim **1** where the silver depositing nuclei are present only in hydrophilic materials.

7. The process of claim **1** where development is with a diffusion transfer developer comprising a developing agent and a solvent for dissolving silver halide.

8. The process of claim **7** where etch-bleaching is with an aqueous etch-bleaching bath comprising an oxidizing agent.

9. The process of claim **8,** wherein said oxidizing agent is peroxosulfate, peroxodisulfate or hydrogen peroxide.

10. The process of claim **1,** wherein said dyestuff is an acid dye and said after treatment is carried out at a temperature of 50° to 90°C.

11. The process of claim **1,** wherein said dyestuff is present in an amount greater than 0.01% by weight of the solution, the pH is alkaline, and the temperature is 2° to 90°C, the treatment period being 5 seconds to 5 minutes.

12. The process of claim **11,** wherein the concentration is 0.5 to about 5%, the pH is 7 to 11, and the temperature is 10° to 50°C.

13. The process of claim **1,** wherein said solution of said dyestuff is an aqueous solution containing also from 2 to 60% based on the solution weight of an organic solvent which is miscible with water.

14. The process of claim **13,** wherein said organic solvent is present in an amount from 2 to 20%.

* * * * *