

[54] **PREPARATION PLATE WITH SILVER  
HALIDE OF PLANOGRAPHIC  
EMULSION COMPRISING  
HYDROPHOBIC THERMOPLASTIC  
POLYMER PARTICLES**

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[57] **ABSTRACT**

An improvement on U.S. Pat. No. 3,476,937 wherein the recording material contains, in addition to a continuous phase of hydrophilic binder and a dispersion phase of thermoplastic hydrophobic particles in a weight ratio relative to the binder of at least 1:1, a light-sensitive silver halide and a developing agent for such halide present in the surface layer and/or in an adjacent underlying layer so that exposure and photographic development by means of an alkaline solution produces a silver image in heat-conductive relationship with the thermoplastic particles and subsequent uniform exposure by the developed silver image, the heat generated in the silver image by such absorption rendering the areas of the surface layer in heat-conductive relationship therewith relatively less hydrophilic.

14 Claims, No Drawings

# PREPARATION PLATE WITH SILVER HALIDE OF PLANOGRAPHIC EMULSION COMPRISING HYDROPHOBIC THERMOPLASTIC POLYMER PARTICLES

The present invention relates to the preparation of planographic printing masters.

Planographic printing is based on the physical properties of repulsion of greasy materials to water. In ordinary planographic printing the printing master surface contains the pattern of the image to be printed in terms of a differentiation in water repellency. The printing plate is usually prepared by imagewise affixing a water-repellent substance or composition, usually greasy, resinous or waxy in nature, to a hydrophilic surface. According to a more recent technique a hydrophilic surface is imagewise converted into a hydrophobic one, by heat-absorption as is described e.g., in the Belgian Patent specifications 656,713 and the cognated United Kingdom Patent application 20,818/65 and 21,985/65.

In ordinary planographic printing use is made of inks that are composed of a lipophilic phase wherein pigments and other suitable ink ingredients are worked up, which does not absorb water or only to a small extent. During printing according to the classical planographic process the printing plate is kept supplied with an aqueous composition so as to keep the nonprinting areas sufficiently hydrophilic. This method of printing thus requires in addition to an inking system a so-called "damping system" by means of which the hydrophilic areas are covered with water or a colorless aqueous composition and thus kept grease-repellent.

According to a more recently developed planographic printing process, called "reversed planographic printing process" use is made of a printing master, wherein the hydrophilic parts constitute the printing parts. The printing ink used in this process contains an aqueous ink composition as colored medium and the damping system is used for applying a colorless oleophilic liquid composition. This printing process is very suitable for direct planographic printing, in other words a process wherein there is no need to reverse the image (offset) by means of an intermediate cylinder with rubber blanket.

Various proposals have been made to record printed matter by irradiating the printed markings so that they become heated while in heat conductive relationship to a heat-sensitive recording material. Certain proposals have also been made to record a pattern of light by exposing to it a recording material which is susceptible to heating and undergoes change in the illuminated areas due to internal absorption of light and conversion thereof to heat energy.

A recording technique wherein a hydrophilic recording material is susceptible to heating and wherein heated portions of a heat-sensitive layer become hydrophobic is described in the Belgian Patent specification 656,713 (corresponding United Kingdom Patent application 48,128/63) and the cognated United Kingdom Patent applications 20,818/65 and 21,985/65. The hydrophilic-hydrophobic differentiation obtained according to the technique described and claimed in said Applications is sufficient for application in the preparation of planographic printing masters.

The present invention is concerned with recording methods utilizing principles as described in the above United Kingdom Patent Applications and contributes to the realization of improved quality planographic prints which are attractive from the standpoint of manufacture and use on commercial scale.

It has now been found a method of preparing a planographic printing master which comprises the following features.

A recording material comprising

a. a heat-sensitive surface layer containing dispersed in a hydrophilic binder thermoplastic hydrophobic particles that are solid at room temperature,

b. light-sensitive silver halide and a developing agent therefor, the light-sensitive silver halide being developable to silver standing in heat-conductive relationship with the thermoplastic hydrophobic particles, is treated as follows:

1. imagewise or informationwise exposed with light to which the silver halide is sensitive,

2. developed with the aid of an alkaline solution,

3. nondifferentially exposed to electromagnetic radiation which effects a heating in the surface layer in accordance with the silver image obtained on development, whereby the layer, which prior to said integral exposure was hydrophilic and water-permeable and contains said hydrophobic particles, becomes in the areas corresponding with the silver image less hydrophilic in a sufficient degree so as to use the thus treated recording material as a planographic printing master, e.g., in reversed planographic printing.

According to a preferred embodiment the surface layer of the recording material contains the hydrophobic thermoplastic particles and the silver halide dispersed in the hydrophilic binder of that layer.

The developing agent is preferably present in the surface layer but may be present in another colloid layer in water-permeable relationship therewith.

In preparing a printing master for reversed planographic printing the imagewise or informationwise exposure is preferably carried out in such a way that after development a laterally reversed silver image is obtained, so that after the integral exposure, which yields the necessary heat for hydrophobizing the surface layer in correspondence with the silver image, a printing master suited for the production of positive prints by direct reversed planographic printing is obtained.

The surface recording layer, which whether or not contains light-sensitive silver halide, for reason of mechanical strength must cohere and therefore contains a sufficient amount of hydrophilic binder for the thermoplastic hydrophobic particles dispersed therein.

According to a preferred embodiment hydrophobic thermoplastic polymer particles, known as latex particles, but being solid at room temperature, are used in the recording layer. For practical useful results the ratio by weight of said particles in respect of the hydrophilic binder should be in excess of 1:1, and more preferably in excess of 3:2. Further, preferably at least 50 percent by volume of the recording material should consist of the dispersion of said polymer particles in the hydrophilic binder.

Latex compositions and hydrophilic binders suited for use in the recording materials applicable in the present invention are described in the Belgian Patent specification 656,713 and the cognated United Kingdom Patent applications 20,818/65 and 21,985/65.

In the preparation of the surface recording layer, the thermoplastic hydrophobic polymer particles, which are solid at room temperature, are dispersed in an aqueous medium preferably already containing the hydrophilic binder and coated in dispersed state at a temperature not substantially higher than room temperature. The polymer particles are surrounded by a wetting or dispersing agent since in the preparation of a latex for dispersing the monomer such a wetting or dispersing agent is always used. The latex particles preferably soften between 10° and 200° C. above room temperature. As examples of suitable latex polymers may be cited such polymers having a melting point or a glass-transition temperature between 10° and 200° C. above room temperature. Particularly suitable polymers are polyethylene and polyvinylidene chloride having a melting point of 110° and 190° C. respectively, and the following polymers with their respective glass-transition temperatures: polystyrene (100° C.), polymethyl methacrylate (comprised between 70° and 105° C.), polyvinyl chloride (near 70° C.), polyacrylonitrile (near 100° C.), and poly(N-vinylcarbazole) (200° C.).

Particulars about the preparation of hydrophobic thermoplastic polymer particles in latex form can be found in the cognated United Kingdom Patent applications 20,818/65 and 21,985/65. It is suitable to use in the recording layers an amount of polymer particles comprised between 0.5 g. and 10 g./sq.m.

In the hydrophobic dispersed phase of the recording layer, alone or together with the latex particles, use may be made of hydrophobic solid substances of waxlike nature or consistency

and preferably having a melting point or melting range between 40° and 120° C.

For that type of particles and combination with a hydrophilic binder particularly reference is made to the United Kingdom Patent application 47,626/66. In the absence of latex particles the ratio by weight of dispersed hydrophobic waxlike particles to hydrophilic binder is preferably at least 1:4 and at most 25:1.

The particle size of the hydrophobic dispersed material preferably lies between 0.01 and 50  $\mu$ .

As hydrophobic solid substances (solid at room temperature) for composing the hydrophobic dispersed phase use may be made of, e.g., paraffins such as petrolatum, solid fatty acids such as stearic acid and adipic acid, alcohols such as lauryl alcohol and n-hexadecyl alcohol, and waxlike substances, so waxes in the broadest sense of the word.

Thus, waxes of the known six classes i.e., vegetable, mineral, insect, petroleum, animal and synthetic waxes may be used.

Carnauba wax, ouricury wax, candellila wax, japan wax, and sugar cane wax, which belong to the vegetable wax class; ozokerite, montan wax, ceresin, and Utah wax, which are mineral waxes, beeswax, and Chinese insect wax, which belong to the insect class; paraffin wax, which is a member of the petroleum class; spermacetic wax from the sperm whale which wax is of the animal class, may be used. These waxes, e.g., ceresin, can be mixed with oil.

Vegetable, insect, and animal waxes are usually composed of a mixture of various high-melting fatty acids, alcohols, and esters.

Chemically modified natural waxes such as the "IG" waxes made from the natural montan wax can also be used. Another modified natural wax is a partly oxidized paraffin that can be a substituted for carnauba wax. Castor wax and Opalwax are waxes obtained from hydrogenated castor oil.

Further synthetic waxes are, e.g., those sold under the trade names Acrawax, Armid, Voltalef, and Carlisle wax.

"Acrawax" is a registered trade mark of Glyco Chemicals, Inc. — New York, N.Y., U.S.A.) for complex nitrogen derivatives of the higher fatty acids.

"Armid" is a registered trade mark of Armour Industrial Chemical Company, Chicago, Ill., U.S.A. for a waxlike material containing fatty acid amides.

"Voltalef" is a registered trade mark of Pechiney — St. Gobain, Paris, France, for chlorine- and fluorine-substituted hydrocarbons.

"Carlisle" is a registered trade mark of Carlisle Chemical Works, U.S.A. for synthetic waxes, the physical constants of which are mentioned in Bennett H.; Industrial waxes, Vol. I, Natural & Synthetic waxes (1963) Chemical Publishing Comp. New York, U.S.A.

Detailed information of many types of waxes can be found in the above-mentioned book of Bennett H., in Albin H. Warth, The Chemistry and Technology of Waxes, 2nd Ed. Reinhold Publishing Corp. New York, and in Rompp H., Chemie Lexikon, Vol. II, Franckh'sche Verlagsbuchhandlung Stuttgart.

Use can also be made of hydrophobic thermoplastic resins, which can be dispersed in an aqueous medium in molten state, and subsequently cooled in finely divided state, e.g., silicon resins, polyethylene, polypropylene, polyisobutylene, polyvinyl stearate, polyhexamethylene adipate, a hydrogenated glyceryl ester of ricinoleic acid, a pentaerythritol ester of stearic acid, and the polyester of sebacic acid and 1,6-hexanediol.

The exposure for obtaining a latent silver image in the recording material may be carried out in any way, e.g. through a transparency (exposure by transmission) or to an opaque original (exposure by reflexion). So, a daylight-sensitive emulsion may be exposed in a camera containing a suited optical system and a less sensitive emulsion exposed in contact with an original in a copying apparatus.

The nondifferential irradiation of the recording material containing the developed silver image provides the necessary heat to hydrophobize the surface recording layer and may proceed by means of infrared and/or visible light. The intensity and duration of that nondifferential irradiation are such that the surface recording layer is struck by a light energy of at least 0.1 Watt.sec./cm.<sup>2</sup>. In order to reduce lateral conduction of heat within the recording material, the nondifferential exposure is preferably very short. Preferably the exposure lasts no more than 10<sup>-1</sup> second and the best results are obtained with exposure times of less than 10<sup>-2</sup> second, e.g., of between 10<sup>-3</sup> and 10<sup>-4</sup> second. Such brief exposure times imply the use of high-energy radiation sources. Preferably the intensity of the light incident upon the recording material is at least 0.1 Watt.sec./cm.<sup>2</sup>.

When using very brief exposure times as above specified, a sharp hydrophilic-hydrophobic differentiation can be obtained.

The shorter the exposure time for a same amount of light energy used in the exposure, the higher the local increase of temperature.

Excellent results are obtainable with exposure times of between 10<sup>-1</sup> and 10<sup>-5</sup> second. Various types of flash lamps are ideally suitable radiation sources for briefly emitting electromagnetic radiation (infrared, visible and/or ultraviolet light). Particularly useful are gas discharge lamps emitting light substantially in the wavelength range of 0.3  $\mu$  to 1  $\mu$ .

Although for reason of extreme copying sharpness a high-intensity short-duration exposure is applied for heating the silver image and the corresponding areas of the surface recording layer, a common infrared light exposure, e.g., in a commercial thermographic copying apparatus, yields a satisfactory result.

In order to obtain a heating corresponding to the silver image as selective as possible the surface-recording layer preferably does not contain, prior to the development of the imagewise exposed silver halide, photochemical inert pigments or dyes that convert light into heat. A restricted amount, however, e.g., up to an optical density of 0.30, of such dyes or pigments does not harm substantially and will help to heat the surface recording layer during its nondifferential exposure. Suitable dyes and pigments for that purpose are mentioned in the cognated United Kingdom Patent applications 20,818/65 and 21,985/65 which applications are to be read in conjunction herewith.

The silver halide used in the present invention is, as already has been said, preferably present in the surface recording layer wherein the desired differentiation in wettability is produced but it may be present in an underlaying colloid layer which stands in heat-conductive and water-permeable relationship with the surface layer.

The type of silver halide does not play a substantial role although for the production of a planographic printing master reproducing graphic information (printed text, line drawings, screen images) a silver halide emulsion of a contrasty type is preferred. The silver halide emulsion may be of the negative or direct positive type (Herschel or solarization effect) and may be sensitive for electromagnetic radiation selected from the group of  $\gamma$ -rays, X-rays, ultraviolet, infra-red and visible light of the whole or part of the visible spectrum. The amount of silver halide per sq.m is preferably comprised between 0.5 g. and 1.5 g. per sq.m.

For use in the preparation of a printing master suited for producing positive prints of an original by direct reversed planographic printing a silver halide emulsion layer of the negative type is imagewise exposed in such a way that by development a negative laterally reversed silver image is obtained.

The recording material contains the necessary developing agent for the silver halide so that it can be developed by a simple treatment with a so-called "activating bath" i.e., an aqueous alkaline solution containing no developing agent. As to the use of an activating bath for the developing of silver halide

emulsion layers suited for the silver halide complex diffusion transfer process reference is made to the United Kingdom Patent Specifications 1,012,476, 1,042,477 and the United Kingdom Patent Applications 4,548/64 and 30,989/63.

The use of the developing agent in the aqueous alkaline solution is also possible but is not preferred from the standpoint of the keepability of the developer on storage and its tendency of being oxidized by air in the developing apparatus.

When an emulsion with a high gradation has to be used, preferably, an emulsion applied in the silver halide complex diffusion transfer technique or a so-called "lith-emulsion" is applied, which emulsions on account of their very contrasty development are very suited for use in the graphic art. As light-sensitive materials suited for the reproduction of graphic line or screen images, lith-emulsions of the silver chloride, silver chlorobromide or silver chlorobromoidide type (normally less than 1 mole percent iodide) are generally employed. For such type of emulsions and an improved development thereof reference is made to the German Patent specification 1,141,531 and the United Kingdom Patent application 41,638/66.

The development of the silver halide emulsion layer may be a hardening development and for such type of development reference is made, e.g., to the United Kingdom Patent specifications 1,049,191 and 1,049,192. If the silver halide is contained in the heat-sensitive surface layer, the mechanical strength and hydrophobicity of the latter in the developed areas will be improved by such a hardening development.

According to the type of silver halide emulsion, i.e., negative or direct-positive emulsions, and to the characteristics required, the silver halide may be combined with spectral sensitizing agents and chemical sensitizing agents such as sulphur-containing compounds, e.g., allylthiocyanate, allylthiourea or sodium thiosulphate, reducing agents such as the tin compounds described in the Belgian Patent specifications 493,464 and 568,687, the imino-aminomethane sulphinic acid compounds described in the British Patent Specification 789,823 or precious metal compounds such as gold, platina, palladium, iridium, ruthenium and rhodium compounds. The silver halide may further be combined with stabilizing agents such as mercury compounds, and the compounds described in the Belgium Patent specifications 571,916 and 571,917 either or not in combination with cadmium salts and stabilizing agents of the azaindene type.

The reversal speed of direct-positive emulsions for use according to the Herschel effect has been increased by a type of dyes which in silver halide emulsions of the negative type act as desensitizers and therefore are called desensitizing dyes (see e.g., C. E. Kenneth Mees, *The Theory of The Photographic Process*, Revised Edition 1954 — The Macmillan Company, New York, p. 263). In that connection reference is particularly made to desensitizing dyes of the nitrotyrlyl and nitrobenzylidene type, representatives of which are described, e.g., in the United Kingdom Patent specifications 667,206, 698,576 and 834,839.

"Desensitizing dyes" for use in direct-positive emulsions whereby the reversal of the image occurs in the short wavelength region of the spectrum are described, e.g., in the United Kingdom Patent specifications 821,251 and 796,873.

Other ingredients such as hardening agents, wetting agents, hydrophilic colloids, latices and plasticizers, may be incorporated into the emulsion in the usual way.

According to an embodiment which is interesting because of its simple processing procedure a heat-sensitive surface recording layer is used containing a silver halide emulsion of the negative type suited for use in document reproduction and which emulsion contains in its turn as developing agent hydroquinone. The development of such emulsion layer is carried out by means of an alkaline aqueous solution (e.g., a 5% aqueous sodium hydroxide) which is supplied to the surface recording layer with a lick-roller and nondifferentially absorbed therein. Immediately after that processing, which is called herein a "monobath" processing, the recording materi-

al is squeezed between two rollers in order to remove a major amount of moisture, whereupon the surface recording layer containing a silver image is nondifferentially irradiated with infrared light produced by the light-source of a common infrared lamp contained in a commercial thermographic copying apparatus. By that nondifferential exposure due to the heat-accumulated in the silver parts the surface recording layer is made hydrophobic in correspondence with the said silver parts.

According to an embodiment that is interesting in the case use is made of light-sensitive silver halide emulsions undergoing a rapid overall fogging after development, e.g., a high-speed silver halide emulsion, a "two-bath" processing can be applied. In such a processing the imagewise exposed recording material is first moistened with the alkaline activator solution whereafter the development is stopped by means of a stop-bath or stabilizing bath. A stop-bath essentially contains an acid for neutralizing the alkali of the activator bath. A stabilizing bath substantially contains a compound transforming light-sensitive silver halide in a nonlight-sensitive or less light-sensitive silver compound. A usual stop-bath contains, e.g., acetic acid and a stabilizing agent, e.g., ammonium rhodanide. An acid fixing bath containing thiosulphate ions may perform both functions of lowering the pH and transforming the non-developed silver halide in a less light-sensitive compound.

In the development step of the processing according to the present invention it is not necessary to develop the emulsion up to the maximum density since already a useful differentiation in wettability for planographic inks can be obtained by irradiating a silver image of a density 0.2. This enables an important decrease of the development time and reduces the possibility of overall fogging of the emulsion in a processing without stop- or stabilizing bath.

It is self-explanatory that when a printing master suited for direct reversed printing is to be produced in the recording material from a negative original, which is e.g., a negative transparency of a printed text, a silver halide emulsion of the direct positive type may be used, which emulsion by development yields a silver image in the unexposed areas. Suited silver halide emulsions of the direct-positive type are described e.g., in the United Kingdom Patent applications 41,638/66 and 20,343/66 which Applications contain information about the preparation, and sensitization of such emulsions.

Printing masters obtained according to the present invention are suited for use in planographic printing with a lipophilic as well as with a hydrophilic printing ink. A hydrophilic printing master prepared according to the present invention is described and claimed in the United Kingdom Patent application 7,800/65 (corresponding Belgian Patent specification 676,898). Said ink is defined as a hydrophilic printing ink composition having dispersed therein a lipophilic phase that is colorless or substantially colorless or of a color tone contrasting with that of the hydrophilic phase, which is colored e.g., with a black pigment.

An hydrophilic ink for use with a said printing master is not necessarily mainly composed of water. In the colored hydrophilic phase hydrophilic water-soluble compounds may be present in a relatively high amount, e.g., up to 80 percent by weight in respect of water, for providing a higher viscosity and a more pastelike consistency to the ink. Hydrophilic compounds that are particularly useful in that respect are water-soluble polyols, e.g., ethylene glycol and water-soluble polyox-yalkylene compounds.

The following examples illustrate the present invention.

#### EXAMPLE 1

A paper supporting weighing 90 g. per sq.m and subbed with a polyethylene layer was coated with a light-sensitive gelatin silver chloride emulsion comprising 0.7 g. of silver, 2.6 g. of gelatin and 0.25 g. of hydroquinone per sq.m.

After drying, the emulsion layer was coated with heat sensitive layer pro rata of 30 g. per sq.m. from a composition comprising:

75 10 % aqueous solution of gelatin

100 ccs.

|                                                                                                                       |          |
|-----------------------------------------------------------------------------------------------------------------------|----------|
| 40 % aqueous dispersion of polyethylene having a particle size of 0.1 $\mu$ and an average molecular weight of 30,000 | 160 ccs. |
| water                                                                                                                 | 660 ccs. |
| 4 % aqueous solution of formaldehyde                                                                                  | 40 ccs.  |
| 5 % aqueous solution of sodium tetradecyl sulphate                                                                    | 50 ccs.  |

After drying, the recording material was exposed reflectographically while in contact with a paper original, conducted through a two-bath apparatus comprising an alkaline bath (5 % aqueous sodium hydroxide) and a stop-bath (6 % aqueous acetic acid).

The heat-sensitive layer of the dried material was then irradiated with an infrared radiation source in a thermographic copying machine "Eichner" on setting 7 (trade name for a thermographic copying machine from Eichner Dry Copy, Frankfurt am Main, W. Germany). The developed metallic silver-containing areas corresponding to the nonimage areas of the original were impermeabilized for water and made hydrophobic, whereas the white areas corresponding to the image-markings of the original remained hydrophilic and receptive for a hydrophilic ink. The resulting master was then braced on the printing cylinder of a planographic printing apparatus for direct printing and inked with an ink composition prepared by adding while stirring:

|                                                                                  |         |
|----------------------------------------------------------------------------------|---------|
| urea                                                                             | 12.5 g. |
| 1,6-hexanediol                                                                   | 40 g.   |
| a 53 % aqueous dispersion of copoly (n-butyl acrylate/vinyl acetate) (72/28)     | 20 g.   |
| 80 % aqueous solution of a melamine formaldehyde resin                           | 37.5 g. |
| triethanolamine                                                                  | 1.5 g.  |
| 30% aqueous solution of copoly(vinyl acetate/crotonic acid ammonium salt) (95/5) | 110 g.  |

to an amount of 250 g. of an aqueous carbon dispersion comprising per 100 g. 53 g. of carbon, 23 g. of water, 18 g. of ethylene glycol, and 6 g. of nonylphenyl polyethylene oxide, adding then 300 ccs. of White Spirit having a boiling range between 140° and 200° C., and mixing the whole composition thoroughly in an ultrasonic mixing apparatus.

#### EXAMPLE 2

A paper support weighing 80 g. per sq. m. was coated with a light-sensitive gelatino silver halide emulsion suited for processing in a two-bath apparatus, in such a way that 0.7 g. of silver, 2.6 g. of gelatin, and 0.25 g. of hydroquinone were present per sq.m.

After drying, the emulsion layer was coated with a heat-sensitive layer pro rata of 50 ccs. per sq.m. from a composition prepared by

1. mixing for 1 hour in a vibratory ball mill:

|                                         |         |
|-----------------------------------------|---------|
| pentaearylthritol ester of stearic acid | 1 g.    |
| Carlisle 325 Wax (melting at 163° C.)   | 5 g.    |
| methanol                                | 40 ccs. |

2. adding to the resulting fine wax dispersion:

|                                                                                    |         |
|------------------------------------------------------------------------------------|---------|
| shellac                                                                            | 2 g.    |
| a petroleum resin consisting of a polydiene with cyclic and acyclic diolefin-units | 2 g.    |
| methanol                                                                           | 40 ccs. |

3. grinding the total bulk for 6 hours in a ball mill.

The resulting light-sensitive and heat-sensitive material was then exposed reflectographically while in contact with an original, developed in the classical way in a two-bath apparatus (alkaline activating bath and stabilizing bath).

The developed material was then exposed briefly to an infrared radiation source, whereby the areas of the heat-sensitive layer above the developed areas of the emulsion layer were impermeabilized for water and became hydrophobic. The nonheated areas remained hydrophilic, so that a laterally reversed printing master was obtained. This master was used

directly for printing on common paper by means of an hydrophilic ink consisting of:

|                                                                                                                                               |          |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----------|
| aqueous carbon dispersion comprising per 100 g.: 53 g. of carbon, 23 g. of water, 18 g. of glycol and 6 g. of nonyl phenyl polyethylene oxide | 100 g.   |
| zein                                                                                                                                          | 13 g.    |
| triethylene glycol                                                                                                                            | 36 ccs.  |
| white spirit (boiling range: 140° to 200° C.)                                                                                                 | 100 ccs. |
| paraffin oil                                                                                                                                  | 20 ccs.  |

Several hundreds of black trueprints could be made in this way.

#### EXAMPLE 3

A paper support weighing 90 g. per sq.m was coated with a light-sensitive and heat-sensitive gelatino silver halide polyethylene emulsion layer in such a way that an amount of silver chloride equivalent to 0.85 g. of silver, 1.7 g. of gelatin, 1.4 g. of hydroquinone and 4.2 g. of polyethylene applied as a 40 percent aqueous dispersion of particles having an average size of 0.1  $\mu$  and an average molecular weight of 30,000 were present per sq.m.

After drying, the material was exposed reflectographically while in contact with a graphic paper original and conducted through a monobath developing apparatus wherein a 5 percent aqueous solution of sodium hydroxide was applied to the exposed layer. Following that treatment the recording material was squeezed between two rollers for pressing the recording material practically touch-dry, whereupon it was nondifferentially exposed to infrared light in a thermographic EICHNER copying machine on setting 7.

The planographic printing master thus obtained was then braced on the printing cylinder of a planographic printing apparatus for direct printing and inked with an ink composition as described in example 1.

#### EXAMPLE 4

A baryta-coated paper weighing 90 g. per sq.m was coated with a light-and heat-sensitive gelatino-silver chloride emulsion pro rata of 50 g. per sq.m from a composition comprising:

|                                                                                                                            |          |
|----------------------------------------------------------------------------------------------------------------------------|----------|
| 5.3 % aqueous solution of gelatin comprising an amount of silver chloride equivalent to a 2.3 % solution of silver nitrate | 375 ccs. |
| 40 % aqueous dispersion of polyethylene having a particle size of 0.1 $\mu$ and an average molecular weight of 30,000      | 125 ccs. |
| 4 % aqueous solution of formaldehyde                                                                                       | 15 ccs.  |
| hydroquinone                                                                                                               | 3 g.     |
| 1-phenyl-3-pyrazolidinone                                                                                                  | 1 g.     |

After drying, the material was exposed and further processed as described in example 3.

The developed metallic silver-containing areas corresponding to the nonimage areas of the original were made hydrophobic, whereas the white areas, corresponding to the image-markings of the original remained hydrophilic and receptive for a hydrophilic ink.

We claim:

1. The preparation of a planographic printing master comprising the steps of

1. exposing to an image of the information to be printed a recording material comprising
  - a. a heat-sensitive surface layer comprising a continuous phase of a hydrophilic binder having dispersed therein thermoplastic hydrophobic polymer particles that are solid at room temperature, said thermoplastic polymer particles being present in a ratio of weight of at least 1:1 relative to said binder, and
  - b. in said surface layer and/or in an adjacent underlying layer a light-sensitive silver halide and a developing agent therefor, the light-sensitive silver halide being developable to silver standing in heat-conductive relationship with the thermoplastic hydrophobic particles,
2. developing the latent silver image in an alkaline solution, and

3. uniformly exposing the developed material to electromagnetic radiation which effects an image-wise heating in the said surface layer as a consequence of the absorption of said radiation by the developed silver image, whereby the recording layer in the areas corresponding with the silver image is rendered less hydrophilic in a sufficient degree as to accept oily printing ink.
2. The preparation of a planographic printing master according to claim 1, wherein said surface layer contains the light-sensitive silver halide and the developing agent.
3. The preparation of a planographic printing master according to claim 1, wherein the silver halide is a part of a silver halide emulsion of the negative type.
4. The preparation of a planographic printing master according to claim 3, wherein the silver halide is a part of a silver halide emulsion suited for the reproduction of graphic information.
5. The preparation of a planographic printing master according to claim 1, wherein the dispersion of said polymer particles in the hydrophilic binder is present in said recording layer for at least 50 percent by volume.
6. The preparation of a planographic printing master according to claim 1, wherein the recording layer contains hydrophobic thermoplastic wax.
7. The preparation of a planographic printing master according to claim 1, wherein the dispersed hydrophobic thermoplastic polymer particles size from 0.01 to 50  $\mu$ .
8. The preparation of a planographic printing master according to claim 1, wherein the silver halide is a part of a direct-positive silver halide emulsion.

9. The preparation of a planographic printing master according to claim 2, wherein the developing agent is hydroquinone.
10. The preparation of a planographic printing master according to claim 1, wherein the uniform exposure of the developed recording material is carried out by means of a lamp emitting infrared light.
11. The preparation of a planographic printing master according to claim 1, with the modification that after the development of the latent silver image, the recording material is treated with a stop- or stabilizing bath.
12. The preparation of a planographic printing master according to claim 1, wherein the recording material after its development is squeezed between rollers in order to remove a substantial part of moisture absorbed in it and thereupon is nondifferentially exposed to electromagnetic radiation which is absorbed in the silver image and converted therein into heat.
13. The preparation of a planographic printing master according to claim 1, wherein a silver halide emulsion of the negative type is exposed with a positive original in such a way that on development a laterally reversed silver image with reversed image values in respect of the original is produced and the resultant planographic printing master is suited for reversed planographic printing.
14. The preparation of a planographic printing master according to claim 1, with the modification that additional developing agent is present in the alkaline solution.

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