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LITHOGRAPHIC OFFSET MASTER AND METHOD

Mary K. Ormsbee and Ruth E. Ormsbee, River Forest,
and Frederick O. Bach, Villa Park, Ill., assignors to
A. B. Dick Company, Niles, Ill., a corporation of
Illinois
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ABSTRACT OF THE DISCLOSURE

A duplicating master and method for producing the master comprising a base sheet characterized by a hydrophobic surface. A nucleated hydrophilic coating is provided on the surface in the non-image areas thereof with the hydrophobic surface of the base sheet being exposed in the image areas. The hydrophilic coating originally covers the entire hydrophobic surface but is characterized by the ability to receive silver halide by diffusion transfer in image areas when an exposed negative is brought into contact with the coating in the presence of a developing solution. Metallic silver is formed in the image areas due to the reduction of the halide thereby enabling the removal of the coating in the image areas.

This invention relates to lithographic or offset masters, to the production of such masters, and to the production of copy therefrom.

In accordance with conventional practice, offset masters are imaged by applying an ink receptive, water repellent, hydrophobic imaging material over a lithographic surface. The lithographic surface is water receptive and comprises the surface of the offset master whereby the master can be wet with an aqueous repellent and with a hydrophobic or oleaginous ink composition. The aqueous repellent wets out the non-imaged portions of the master so that when the master is engaged by an ink roller containing an ink composition, the water wetted non-imaged portion will repel ink while the unwetted, ink receptive imaged portions receive ink for subsequent transfer to copy sheets by direct or offset processes.

Various conventional methods are employed for applying the hydrophobic image areas over the hydrophilic lithographic surface. This invention relates to a system wherein an original such as a printed page can be utilized in a system whereby a direct reproduction of the material on the original can be imaged on a master sheet. The master sheet can then be utilized for the production of multiple copies of the original, and the invention is particularly characterized by simplicity and efficiency in the production and use of the master.

The systems of the instant invention specifically involve the utilization of diffusion transfer processes. The diffusion transfer process is described relative to the production of single copies in the Rott Patent No. 2,352,014. In the single copy process described therein, a photographic image of an original produced in a silver halide layer is caused to produce a reverse image on a copy sheet, provided the silver halide layer, after being exposed to light for the production of a latent image and then being impregnated with a developer to develop the image, is pressed or squeezed in the presence of a

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fogging agent and a solvent for the silver halide onto the copy sheet while the layer is still imbedded with the developing liquid. That part of the silver halide in the layer which is not reduced during development of the exposed negative and which, in the ordinary photographic process, would be fixed out in the fixing bath will transfer by diffusion to the surface of the copy sheet to provide a reverse image thereon. In order to render this image freely visible, the light-sensitive layer containing the master image will normally be removed from the copy sheet.

In the Rott process, use can be made of the silver halide solvent contained in the usual photographic developers, such as sodium sulfite, sodium thiosulfate and the like. As fogging agents, use is made of a substance capable of promoting the reduction of silver halides without requiring the action of light, such for example as colloidal silver, colloidal forms of sulphur, silver sulfides, hypophosphites, stannous chloride, and organic compounds which are capable of splitting off sulphur in the form of bivalent ions, as represented by thiosinamine and thiocyanates. Such fogging agents are preferably embodied in the copy sheet during the manufacture thereof or they can otherwise be incorporated by a subsequent coating or impregnation.

It is an object of this invention to provide an improved offset or lithographic master and an improved procedure for the preparation and utilization thereof.

It is a more particular object of this invention to provide an offset or lithographic master which is produced from an original through the use of diffusion transfer techniques.

These and other objects and advantages of this invention will appear hereinafter and it will be understood that the specific embodiments of the invention set forth herein are provided solely for purposes of illustration and not by way of limitation.

The duplicating master of this invention generally comprises a base sheet characterized by a hydrophobic ink receptive surface. A nucleated hydrophilic coating is adapted to overlie the hydrophobic surface and this coating is characterized by the ability to receive silver halide by diffusion transfer when an exposed negative is brought into contact with the coating in the presence of a developing solution. The subsequent reduction of the halide to metallic silver in the image areas permits the removal of the coating in these areas to thereby expose the underlying ink receptive hydrophobic surface. Thereafter, the non-imaged portions of the master can be wetted with an aqueous repellent while the unwetted ink receptive imaged portions are adapted to receive an ink composition. The master is then suitable for the transferring of ink to copy sheets by direct or offset procedures.

In accordance with this invention, the coating overlying the hydrophobic surface may contain a gelatin component. With such an arrangement, the subsequent removal of the coating may be accomplished by an etching operation with a solution which contains an oxidizing agent for softening the gelatin in the presence of the metallic silver or silver complex image areas and thereby facilitate removal of the coating to expose hydrophobic portions of the master.

Other hydrophilic ink repellent film formers can be employed as the coating on the master sheet. The formation of metallic silver in the image areas during the develop-

ing phase operates to physically weaken certain film formers in the image areas. Where the films contain a water soluble component, the removal of the films from the image areas can be accomplished by a washing operation. It is not necessary that the silver actually dissolve in the washing solutions.

The instant invention also contemplates the use of film formers which are water insoluble. In such a case, standard offset etches can be used to remove the hydrophilic water insoluble film for exposing the hydrophobic base in the image areas.

In the formation of the master having the hydrophobic surface, it will be appreciated that various approaches can be taken. The hydrophobic surface may be provided by means of a coating applied over the surface of any base material. On the other hand, a material which is naturally characterized by the necessary hydrophobic properties can obviously be used. In either case, the hydrophilic ink repellent coating or film will be applied over the hydrophobic surface.

In the preparation of the masters of this invention, a conventional photonegative containing a light sensitive silver halide is exposed to an original by reflex or printing through contact or by projection printing to form a latent image in the silver halide coating.

The exposed photographic negative is of a type adapted to be developed in accordance with conventional techniques by means of normal developing components employed by the photographic art. In such development, a silver halide or silver halide complex is formed and the following mono-bath developer is typical of conventional solutions employed for such purposes in photographic practice:

	Grams
Potassium bromide	0.5
Hydroquinone	15
Sodium hydroxide	10
Sodium sulfite (preservative)	70
Sodium thiosulfate (silver halide solvent)	12
Phenidone	1.5
Water sufficient to make up 1 liter.	

The procedure following the exposure of the negative provides for the engagement of the exposed negative with the hydrophilic ink repellent coating on the master. One or both of the surfaces of the master and the negative is wet with a developing solution. In the preferred practice of the invention, the exposed negative and the master will be run together into a bath of the developing solution and then brought into contact with each other between squeeze rolls as the sheets issue from the developing solution.

As the surfaces of the negative and the master are brought into contact with each other during development, the soluble silver complex formed of the silver halide present in the unexposed portions of the negative coating transfers by diffusion to the corresponding areas in the hydrophilic ink repellent coating on the master. It is preferred that conventional means be provided for maintaining contact between the negative and master for a length of time from five seconds up to about two minutes for adequate transfer.

The procedure described provides for the reduction of the silver halide in the image areas of the master to produce a silver image or silver complex image. Thereafter, procedures are employed for the removal of the coating in these image areas whereby exposure of the underlying hydrophobic surface can be accomplished. In this connection, the following examples provide illustrations of specific means for carrying out the formation of the masters in accordance with the above described recitations:

EXAMPLE I

Cellulose acetate film was coated with the following formulation:

Parts by weight

	Gelatin	3.60
	Water	84.80
	Methanol	9.00
5	Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$)	0.05
	Ammonium thiosulfate	0.10
	Resorcinol	0.30
	2,4-dihydroxybenzaldehyde	0.05
	Silver nitrate	0.10

10 An image was transferred by diffusion transfer reversal procedures from a negative while employing the developer previously set forth. The image areas were thereafter etched out employing Kodak "EB-2" etch solution. This etch solution was prepared by dissolving 750 cc. 15 water, 120 grams copper sulfate, 150 grams citric acid and 7.5 grams potassium bromide in water in amounts to make up 1 liter. In a separate container, a solution is formed containing about 3 percent hydrogen peroxide. The 20 two compositions are mixed to form a composite etch solution through which the processed sheet is passed. The etch solution operates to degrade (probably by reaction with the silver and gelatin in the imaged areas) and remove the gelatin in the imaged areas while it has practically no effect upon the hardened gelatin in the non-imaged 25 areas so that the latter will remain as a coating on the base. The processed base is treated by passage through the etch solution subsequent to its separation from the exposed negative.

30 The product obtained comprised a sheet having hydrophobic ink receptive portions (the exposed acetate film) surrounded by hardened gelatin which remains in a hydrophilic state.

EXAMPLE II

A baryta coated photographic paper was provided with an additional coating of the following formulation:

	Parts by weight
Ludox LS (colloidal silica-30% solids) (Du Pont)	50.00
40 Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$)	0.06
Distilled water	25.00
Silver nitrate	0.085

45 A silver image was transferred onto the coated paper in the usual manner. Upon being subjected to an etch solution, portions of the paper were exposed to provide hydrophobic ink receptive image areas while the surrounding areas remained hydrophilic.

EXAMPLE III

50 A conventional water resistant photographic paper was coated with the following formulation:

	Parts by weight
Ludox LS (30% solids) (Du Pont)	30.0
55 Pollectron 130 (polyvinyl-pyrrolidone/ethyl acrylate) (Gen. Aniline & Film)	3.0
Distilled water	25.0
Sodium sulfide (0.5% solution in water)	8.0
Lead acetate (5.0% solution in water)	0.7

60 After transfer to form a silver complex image, Kodak "EB-2" etch solution was employed to etch out the image thus exposing the hydrophobic paper.

EXAMPLE IV

65 2 mil Kodacel TA404 (cellulose tri-acetate film) was coated with the following formulation after thinning of the formulation to a suitable viscosity for coating purposes:

	Parts by weight
70 Daran 202 (vinylidene chloride polymer latex, 60% solids) (Dewey & Almy Div. W. R. Grace Co.)	33.3
Ludox HS (aqueous dispersion of amorphous silica) (Du Pont)	66.7
75 Silver nitrate	0.02

Again a silver image was formed and the plate was etched with A. B. Dick offset etch No. 4-1014 comprising an aqueous solution including glycerine, sodium phosphate, phosphoric acid and alcohol.

EXAMPLE V

3 mil Kodacel TA404 film was coated with the following formulation:

	Parts by volume
5% solution Gantrez AN119 (poly methyl vinyl ether/maleic anhydride resin) (Gen. Aniline & Film) in water	4
Serfene H30 (poly vinylidene chloride latex) (60% solids) (Morton Chemical)	6
Ludox HS (30% solids) (Du Pont)	45
Distilled water	45
5% solution of Saponin (Eastman Chemical) in water	5
Silver nitrate (1.7% solution in water)	6

An exposed negative was contacted with the coated film for transfer of the silver image in the usual manner. A. B. Dick offset etch No. 4-1014 was employed to provide for exposing of the hydrophobic image areas.

It will be appreciated when considering the above examples that a variety of formulations can be utilized provided these formulations are hydrophilic in nature and provided the formulations retain this characteristic after portions thereof have been etched away to expose underlying hydrophobic areas. It is preferred that relatively thin films of the hydrophilic coatings be employed to facilitate removal subsequent to the diffusion transfer phase of the operation. In general, the coating weights preferably average less than one pound of solids per 3000 square feet with a general range being between 0.5 pound to two pounds per 3000 square feet.

As previously explained, the films may be of the gelatin type whereby reaction with an oxidizing agent will condition the gelatin for removal from the image areas. In addition, water soluble ingredients can be employed in the film for removal by washing with water, however, water insoluble films are also clearly suitable since various etching formulations will be suggested to those skilled in the art.

The base carrying the hydrophobic surface can be any of several readily available materials as suggested by the examples. Some materials, such as cellulose acetate, have suitable hydrophobic characteristics while other materials, such as certain conventional photographic papers, can also be utilized with a high degree of efficiency.

The offset masters produced in accordance with the techniques of the instant invention have been successfully used on offset processes with the production of sharp and consistent copy. Since the masters can be produced by simple techniques and with readily available materials, it is obvious that the instant invention can provide substantial savings when compared to other techniques for the production of offset masters.

It will be understood that various changes may be made in the techniques described herein which provide the characteristics of this invention without departing from the spirit thereof particularly as defined in the following claims.

That which is claimed is:

1. A duplicating master comprising a base sheet having a hydrophobic surface, a nucleated hydrophilic coating overlying the non-image areas of said surface, said hydrophobic surface being exposed in the image areas, said coating being characterized by the ability to receive silver halide by diffusion transfer in image areas when an exposed negative is brought into contact with said coating

in the presence of a developing solution for the negative, metallic silver being formed in said coating due to the reduction of said halide resulting from reaction with said developing solution thereby enabling the removal of said coating in said image areas.

2. A duplicating master in accordance with claim 1 wherein said coating contains gelatin whereby an etch solution including an oxidizing agent can be applied for softening of the gelatin in the presence of the metallic silver to thereby remove the coating in the image areas.

3. A duplicating master in accordance with claim 1 wherein said coating comprises a thin, relatively porous film containing a water soluble component, and wherein the formation of metallic silver in the image areas during the developing operates to physically weaken the film in the image areas to thereby enable removal of said film from the image areas by washing of the master with an aqueous solution.

4. A duplicating master in accordance with claim 1 wherein said coating comprises a thin, relatively porous water insoluble film adapted to be removed from image areas on the master by means of an etching solution.

5. A duplicating master in accordance with claim 1 wherein said hydrophobic surface is provided by means of a coating disposed over the surface of a base sheet.

6. A duplicating master in accordance with claim 1 wherein said base sheet is characterized by hydrophobic properties to thereby provide said hydrophobic surface.

7. A method for the formation of a duplicating master comprising the steps of providing a base sheet having an ink receptive hydrophobic surface, applying a coating over said surface comprising a nucleated hydrophilic material, said coating being characterized by the ability to receive silver halide by diffusion transfer when an exposed negative is brought into contact with said coating in the presence of a developing solution for the negative, said transfer taking place in positive image areas on said master and metallic silver being produced in said positive image areas, and removing said coating from said sheet in said image areas to expose the hydrophobic ink receptive surface in said image areas.

8. A method in accordance with claim 7 wherein said coating contains gelatin and wherein said etch solution includes an oxidizing agent for softening of the gelatin in the presence of the metallic silver.

9. A method in accordance with claim 7 wherein said coating comprises a thin, relatively porous film containing a water soluble component, and wherein the formation of metallic silver in the image areas during the developing operates to physically weaken the film in the image areas to thereby enable removal of said film from the image areas by washing of the master with an aqueous solution.

10. A method in accordance with claim 7 wherein said coating comprises a thin, relatively porous water insoluble film adapted to be removed from image areas on the master by means of an etching solution.

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NORMAN G. TORCHIN, *Primary Examiner.*

70 J. P. BRAMMER, *Assistant Examiner.*

Notice of Adverse Decision in Interference

In Interference No. 96,988 involving Patent No. 3,385,701, M. K. Ormsbee, R. E. Ormsbee and F. O. Bach, LITHOGRAPHIC OFFSET MASTER AND METHOD, final judgment adverse to the patentees was rendered Oct. 27, 1972, as to claims 1, 4, 5, 7 and 10.

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