United States Patent

Groncki

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[54] **PRETRANSFERRED SILVER DEPOSIT RECEIVING ELEMENT**

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[52] U.S. Cl. **96/29,** 96/76, 96/33

[51] Int. Cl. **G03c 5/54**

[58] Field of Search 96/29, 76, 38

[56] **References Cited**

UNITED STATES PATENTS

3,220,837 11/1965 Land et al. 96/33

3,344,741 10/1967 Ormsbee 96/29

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[57] **ABSTRACT**

Photomechanical procedures for forming ink reproductions from an inking master obtained by silver diffusion transfer whereby continuous tone subject matter is reproduced to provide ink reproductions thereof of improved tonal quality.

6 Claims, No Drawings

PRETRANSFERRED SILVER DEPOSIT RECEIVING ELEMENT

BACKGROUND OF THE INVENTION

Procedures for preparing photographic images in silver by diffusion transfer principles are well known in the art. In a typical procedure of this nature, an exposed light-sensitive silver halide emulsion containing a developable image is developed with an aqueous alkaline processing composition including a silver halide developing agent and a silver halide solvent to reduce exposed silver halide to silver while forming from unexposed silver halide an imagewise distribution of soluble silver complex which is then transferred, at least in part, by imbibition, to a superposed image-receiving layer where it is reduced to image silver to impart thereto a positive silver transfer image. Procedures of this description are disclosed, for example, in U.S. Pat. No. 2,543,181, issued to Edwin H. Land. The image-receiving layer or silver-receptive stratum, as it is often called, may typically provide one of the vigorous silver precipitating environments such as described in U.S. Pat. Nos. 2,698,237 and 2,698,245 issued to Edwin H. Land.

It has heretofore been known that a silver transfer image obtained by silver diffusion transfer procedures such as described above may be employed as a printing master to obtain one or more ink reproductions of the original subject matter.

One particularly useful procedure for obtaining a printing master by silver diffusion transfer is described in U.S. Pat. No. 3,220,837, issued to Edwin H. Land and Meroe M. Morse. This patent is predicated upon the discovery that if the silver transfer print has areas that contain silver concentrated primarily at the surface of the silver-receptive stratum in thin but essentially continuous, dense masses and other areas that are substantially silver free or which do not contain these dense masses of silver, the areas containing these dense silver deposits are oleophilic and hence are inkable or wettable with an oleophilic ink; whereas the other areas which are initially hydrophilic retain their hydrophilic character and hence are not so inkable. In other words, a silver transfer print of this description is characterized as being such that when an oleophilic ink is applied uniformly over the surface of the print, this ink adheres only to the areas of dense silver deposits, so that the silver transfer image may be characterized further as being selectively inkable with an oleophilic or greasy ink of the type commonly employed in lithography. Thus, following application of the oleophilic ink, the inked silver transfer image may be employed in standard lithographic procedures to provide one or more ink reproductions of the original subject matter.

The copending application of Edwin H. Land, Ser. No. 676,510, filed Oct. 19, 1967, describes and claims another system for forming a printing master by silver diffusion transfer. In the procedures described in this copending application, the image-receiving element employed to prepare the print comprises a silver-receptive stratum having a plurality of layers containing progressively increasing concentrations of silver precipitating nuclei as the distance from the surface increases, the greatest concentration of silver precipitating nuclei being in the layer closest to the hydrophobic support or underlayer containing the silver-receptive stratum. In silver diffusion transfer processes employing such an image receiving element, the silver is deposited deeper into the receiving layer than is obtained in processes such as those described in the aforementioned patent wherein the silver is deposited primarily at the surface of the silver-receptive stratum. In accordance with the procedures disclosed in the aforementioned copending application, development is effected in the presence of an antiadhesion reagent and following silver image formation, the areas of dense silver deposit and corresponding areas of the silver-receptive stratum are selectively removed to provide an intaglio or etched image in terms of this imagewise removal of silver and corresponding areas of the silver-receptive stratum. This image may then be selectively linked with an oleophilic ink which selectively adheres to the hydrophobic underlayer in areas where the silver deposit and silver-receptive stratum have been removed.

By way of recapitulation, in the system described in the patent, selective inkability is obtained by a silver transfer process in which silver halide is transferred to form a silver image wherein the transferred silver is concentrated primarily at the surface of the silver-receptive stratum in thin, but essentially continuous dense masses which are oleophilic; whereas in the system described in the aforementioned copending application the transferred silver is deposited deeper in the silver-receptive stratum, rather than primarily at the surface, and these dense silver deposits and corresponding areas of the silver-receptive stratum are then removed to render the hydrophobic underlayer in these areas selectively inkable.

Common to each of the foregoing systems for preparing inking masters is that selective inkability is obtained by transfer of silver in an amount sufficient to produce areas which are oleophilic, and hence wettable by a greasy ink, as contrasted with the hydrophilic silver-receptive stratum to which it is transferred and which is not so wettable or inkable.

In either of the foregoing procedures ink reproductions having the appearance of continuous tone, i.e., ink reproductions having intermediate gradations of density in so-called "gray areas," may be obtained with the aid of a halftone screen. The use of halftone screens for reproducing photographs or the like having these intermediate gradations is well known in the lithographic art. Such a screen may, for example, comprise two sheets of glass, the adjacent surfaces of which are ruled with fine parallel lines, the lines of one face being perpendicular to the lines of the other to provide a fine grating. These uniformly spaced lines may typically range from 45 to 500 per inch. When a photosensitive element is exposed to continuous tone subject matter through such a screen, the intermediate gradations are typically reproduced as tiny dots. These intermediate gradations so reproduced on the positive silver print (inking master) as tiny dots corresponding to partially exposed areas of the exposed photosensitive element or "gray areas" of the original subject matter, are either of sufficient density to be wetted by an oleophilic ink and hence reproducible, or they are not and the master does not become inked in these areas. In other words, in offset printing techniques employing printing masters of the type to which this invention is directed, the silver is deposited in such a manner that it could be stated to be characterized as a "go—no go" silver deposit. Simply speaking, these areas are either inkable or they are not inkable. If they are not inkable, these gray areas appear on ink reproductions obtained therefrom as highlight or white areas. It will, therefore, be appreciated that such ink reproductions do not possess or exhibit the complete tonal scale of the original subject matter.

Thus, where it is desired to obtain ink reproductions of original subject matter having intermediate gradations over a large range varying in the scale from black to white, it has been found that in the "lighter" of these areas, sometimes insufficient silver is deposited to render these areas inkable so that the resulting ink reproductions are not always of the optimum desired full tonal scale.

It is to this problem to which the present invention is directed.

SUMMARY OF THE INVENTION

The aforementioned objectives are accomplished by providing as the printing master a halftone silver print characterized as having higher D_{min} or greater silver deposits in terms of highlight and partially exposed areas than that which one would normally desire in a silver image. More specifically, according to the present invention, halftone silver images capable of providing ink reproductions having greater intermediate gradations and hence of fuller scale tonal quality are obtained by employing as the silver-receptive stratum a layer to which a uniform "pretransfer deposition" of a small amount of silver

has been made, so that the silver-receptive stratum employed in the silver diffusion transfer process to form the printing master is characterized as processing a substantially uniform silver deposit of a density insufficient in and of itself to render this stratum inkable with an oleophilic ink. When a silver transfer image is formed on such an image-receiving element, whereas the highlight areas are still not inkable, so-called light-gray areas possessing little transfer silver, the amount of which would also not in and of itself be inkable, are now rendered inkable. In other words, the sum total of the pretransfer silver deposition and the silver deposited by the silver transfer process is sufficient to render these areas inkable, whereas either silver deposit alone is not.

As was mentioned previously, the present invention relates to photomechanical reproduction, and more particularly to the preparation of printing masters by silver diffusion transfer photography.

A primary object of this invention, therefore, is to provide novel photomechanical reproduction or lithographic systems of the foregoing description.

Another object is to provide halftone silver images which may be employed as printing masters to obtain one or more ink reproductions of continuous tone subject matter characterized as possessing fuller tonal scale quality.

Still another object is to provide a novel system for preparing silver transfer images wherein a substantially uniform amount of silver is deposited on a hydrophilic silver-receptive stratum the amount of this silver deposit being insufficient to alter the hydrophilic character of this stratum; and a silver transfer image is thereafter formed on this stratum by exposing through a halftone screen a photosensitive element comprising a light-sensitive silver halide layer and applying an aqueous alkaline processing composition to the thus exposed element to develop this image while at substantially the same time forming from unexposed silver halide a water-soluble silver complex which is then transferred by diffusion to this silver-receptive stratum to impart thereto a positive silver transfer image.

Other objectives of this invention will in part be obvious and will in part appear hereinafter.

This invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description. e.g.,

As was mentioned previously, this invention is directed to the preparation of halftone ink reproductions by processes utilizing as the printing master a photographic print obtained by silver diffusion transfer, and it has for its primary objective providing fuller scale tonal reproductions from such printing masters. It has been found that when continuous tone subject matter is exposed and then developed to form a silver image useful as a printing master by diffusion transfer procedures such as are disclosed in the aforementioned U.S. Pat. No. 3,220,837, and copending application Ser. No. 676,510, in the lesser gradations of partially exposed areas, at times insufficient amounts of silver are transferred to provide the optimum desired inkability. These shadow areas therefore appear on the ink reproductions obtained therefrom as highlight or white areas.

It has further been found that the desired inkability may be accomplished to extend the range of inkable areas of the master and hence produce more accurate fuller scale tonal reproductions by employing as the silver-receptive stratum in such photographic systems a silver-receptive stratum which has been previously subjected to a substantially uniform "pretransfer deposit" of silver to provide thereon a silver deposit insufficient in and by itself to alter the hydrophilic character of this stratum. Since an image-receiving element containing a silver-receptive stratum subjected to such a pretransfer silver deposition is light gray in appearance, for east of identification it has been termed a "gray sheet" and will be so designated hereinafter.

The gray sheets of this invention may be formed by applying over the surface of the silver-receptive stratum a solution containing a silver complex soluble therein in an amount sufficient to provide a silver deposit which, as heretofore noted, does not alter the hydrophilic character of the stratum in which it is deposited by rendering it wettable by a greasy ink. Any small silver deposit not so altering the hydrophilic character will produce at least some beneficial results and hence the lower range of silver density so obtained is not critical. The upper range criticality is determined by that amount of silver so deposited taken in conjunction with the D_{min} or unwanted silver in highlight areas obtained in the diffusion transfer process which would alter these highlight areas inkable. In other words, the upper range is so precalculated as to be at some point below the amount which, in the particular photographic system and specific processing conditions in which it is employed, would render the highlight areas of the print inkable. This will, of course, vary to some degree according to the particular photographic process employed and accordingly it will be appreciated that this upper range or limitation is not capable of absolutely precise definition. However, one skilled in the art would readily know, in the light of this description, how to determine the precise ranges of silver to form the gray sheet. In general, this gray sheet may be formed by depositing silver at a reflection density of from about 0.05 to about 0.3.

The image-receiving elements employed to prepare these gray sheets are those of the type heretofore known in the art and employed to prepare printing masters by the aforementioned silver transfer techniques.

In general, the image-receiving element comprises at least a hydrophilic silver-receptive stratum disposed on a suitable layer or support. The silver-receptive stratum preferably comprises a macroscopically continuous vehicle or matrix of a hydrophilic inorganic material, e.g., a siliceous material. Thus, the silver-receptive stratum preferably comprises a matrix formed of definite particles which are essentially silica and which are sufficiently small to be indistinguishable as particles by the naked eye when formed into a layer and whose minimum average size is of colloidal rather than of molecular proportions. The siliceous material comprising this matrix may contain, in colloidal or finely divided condition, oxides of silicon, particularly those in the form of silica acids like silica aerogel, and mineral silicates such as mica and talc. As examples of useful siliceous materials, mentioned may be made of "Syton" (trademark of Monsanto Chemical Co. for a milky-white, stable 15 percent colloidal dispersion of silica in water, sp. gr. 1.10); "Santocel" (trademark of Monsanto Chemical Co. for a lightweight porous silica aerogel from which the water has been removed by a process that does not destroy the original gel structure, apparent density, 6.5–9.75 lb./cu. ft.); and "Ludox" (trademark of E. I. duPont de Nemours & Co. for an aqueous colloidal sol containing approximately 30 percent SiO_2 with less than 0.5 percent Na_2 as stabilizer, sp. gr. 1.21).

The silver-receptive stratum preferably further includes silver-precipitating nuclei providing a vigorous silver precipitating environment for facilitating reduction of silver halide transferred thereto to image silver. As examples of silver-precipitating nuclei, mention may be made of heavy metal sulfides and/or selenides, the colloidal noble metals, organic thio compounds, etc. Suitable silver-receptive strata comprising silver-precipitating nuclei dispersed in a hydrophilic matrix, e.g., a siliceous material, are disclosed, for example, in U.S. Pat. Nos. 2,698,237, and 2,698,245 issued to Edwin H. Land.

In the system described in U.S. Pat. No. 3,220,837, this silver-receptive stratum is such that the silver is deposited primarily at the surface of the stratum. In the system described

in the aforementioned application Ser. No. 676,510, the silver-receptive stratum comprises a plurality of layers containing progressively increasing concentrations of silver-precipitating nuclei as the distance from the surface increases, the greatest concentration of silver-precipitating nuclei being in the layer closest to the support or underlayer containing the silver-receptive stratum. Image-receiving elements of this latter description are disclosed, for example, in the copending application of Edwin H. Land, Ser. No. 622,133, filed Mar. 10, 1967.

In either case, the silver-receptive stratum may be contained on a suitable base sheet or support, e.g., paper, glass or plastic, and various layers performing specific desired functions may be disposed between this stratum and the support and/or over the stratum. By way of example, a layer of a hydrophobic material and/or a layer of an optical brightener may be disposed between the support and the silver-receptive stratum and/or a stripping layer to facilitate clean separation of the print following processing may be disposed over the silver-receptive stratum. In any event, the exact structure and composition of the image-receiving element comprising the silver-receptive stratum per se comprises no part of the present invention.

The silver halide employed to prepare the gray sheet may be any of those, including the mixed halides, commonly employed in the photographic art to prepare light-sensitive silver halide layers. A preferred method of preparing the gray sheet is to apply a composition containing this silver halide over the surface of the image-receiving element and there reducing it to produce the desired silver deposit.

Such a composition may, for example, comprise an aqueous solution including the silver halide, a silver halide solvent and a reducing agent. The silver halide solvent may be any of the silver halide solvent-fixers heretofore employed in the photographic art, e.g., sodium, potassium or ammonium thiosulfate, sodium, potassium or ammonium thiocyanates, organophosphines such a methyl-bis-(2-carboxyethyl) phosphine, methyl-bis-(3-hydroxypropyl) phosphine, etc. The reducing agent employed may be a discriminating silver halide developing agent, e.g., a dihydroxybenzene, diaminobenzene or aminophenol silver halide developer, a nondiscriminating developer or any of the other known reducing agents capable of reducing the silver complex to image silver to provide the gray sheet. As will be apparent to those skilled in the art, the pH of this solution should be adjusted in accordance with the particular solvent-fixer and/or reducing agent employed. With systems using a thiosulfate solvent-fixer and a silver halide developing agent of the character mentioned above, e.g., hydroquinone, an alkaline pH should be provided by the addition of an alkaline material, e.g., sodium or potassium hydroxide, etc. If found desirable or expedient, the composition may also include other reagents, e.g., a viscous reagent such as hydroxyethyl cellulose, carboxymethyl cellulose, etc.

One useful method for forming a solution of the foregoing description is to contact an unexposed or partially exposed light-sensitive silver halide layer in the dark with an aqueous alkaline solution containing at least one silver halide developer and silver halide solvent to form a solution of soluble silver complex and transferring this solution, by diffusion, to the image-receiving element to form the gray sheet. As will be apparent, the amount of silver so transferred and deposited may be regulated to provide the desired density by such known factors as selection of the necessary ingredients of the solution and their proportions, diffusion or imbibition times, etc. Such factors are well known in the photographic art and need not be discussed in further detail.

The gray sheets contemplated herein may be employed as the image-receiving element in the aforementioned silver transfer photographic procedures for forming a printing master to accomplish the objectives of this invention. Therefore, the preparation of a printing master in accordance with this invention comprises the steps of (1) first forming the gray sheet or image-receiving element comprising a silver-receptive stratum containing the silver deposit in an amount as described previously; (2) exposing a light-sensitive silver halide layer through a halftone screen to the subject matter to be reproduced, i.e., continuous tone subject matter such as a person, scenery, etc., to form a developable image; and (3) thereafter developing this image to form a silver transfer image on the gray sheet, in turn forming the printing master which may then be employed in the usual manner to produce halftone ink reproductions of the original.

More specifically, in systems of the type described in U.S. Pat. No. 3,220,837, the gray sheet is of the type previously described which is adapted for forming a dense silver image primarily at the surface, the selective inkability being predicated upon the oleophilic character of the transfer silver so deposited, as distinguished from the hydrophilic silver-receptive stratum. In such a system, the photoexposed silver halide layer is developed by spreading an aqueous alkaline processing composition including a silver halide developing agent and a silver halide solvent to develop exposed silver halide and to form an imagewise distribution of a soluble silver complex which is transferred, by diffusion, to the gray sheet to impart thereto a positive silver transfer image which may then be employed in standard lithographic procedures to provide one or more ink reproductions.

For use with the lithographic systems disclosed in Ser. No. 676,510, on the other hand, the gray sheet is of the type which permits of deeper silver deposits, as heretofore discussed, and the silver image formation is as described in the preceding paragraph, the essential difference being that the image is formed in the presence of an antiadhesion reagent, e.g., a wetting agent, sequestering agent or detergent, and the silver-receptive stratum is then contacted with an aqueous medium, e.g., by lightly swabbing, to remove dense silver deposits and corresponding areas of the silver-receptive stratum to form the printing master.

It is interesting to note that the silver transfer images obtained by the practice of this invention by design or intent have "dirty" highlight areas or an intentionally higher D_{min} than would be ordinarily desired in a silver transfer print and hence would not normally be termed as aesthetically acceptable a photographic image as those obtainable with the same processing conditions on a standard receiving element. However, it is because of this higher D_{min} that the resulting silver image is capable of more faithful reproduction of continuous tone subject matter having varying intermediate gradations in the shadow areas.

The following examples show by way of illustration and not by way of limitation the practice of this invention.

EXAMPLE 1

A gray sheet was prepared by spreading between a silver halide layer of a conventional photosensitive element which had been exposed to a low intensity of light and the image-receiving element from a Polaroid Type **107** Land film at a gap of about 0.0026 a processing composition comprising the following proportions of ingredients:

Water	16,500.0 cc.
Hydroxyethyl cellulose	650.0 g.
Sodium sulfite	425.0 g.
Sodium hydroxide	831.0 g.
Tertiary butyl hydroquinone	503.0 g.
2,4-diamino-o-cresol	37.8 g.

After an inbibition period of 10 seconds, the respective elements were separated to provide a gray sheet having a substantially uniform silver reflection density of 0.3.

EXAMPLE 2

A high-speed silver iodobromide emulsion from a Polaroid Type **51** Land film was photoexposed to continuous tone subject matter through a halftone screen having approximately 120 lines per square inch. Following exposure, a silver transfer

print was obtained by spreading between the thus exposed emulsion and a gray sheet as prepared in example 1 a processing composition comprising the following proportions of ingredients:

Water	8,289.0 cc.
Hydroxyethyl cellulose	366.0 g.
Sodium sulfite	260.0 g.
Sodium hydroxide	425.0 g.
Sodium thiosulfate	741.0 g.
6-nitrobenzimidazole	10.8 g.
2,6-dimethyl-p-aminophenol	270.0 g.
Potassium iodide	15.0 g.
Monobasic ammonium phosphate	45.0 g.

After an imbibition period of about 10 seconds, the image-receiving element was separated to reveal a dense silver transfer image characterized visually as having a relatively high D_{min} and "dirty" highlight areas. This image was rubbed very lightly with a wet facial tissue to form the printing master which was then inked with a standard black greasy ink. From this inked master a halftone ink reproduction was prepared, the tonal quality of which demonstrated the efficacy of this invention.

In the foregoing description mention has been made of applying a silver halide solution to the image-receiving elements as the means of forming the gray sheet. However, it is to be expressly understood that other means of formation are also contemplated. For example, it is within the scope of this invention to form the uniform silver deposit in situ at some time during or after applying the silver-receptive stratum on the image-receiving element. One way of accomplishing this would be to include a reducible silver salt, e.g., a silver halide, in the coating solution and then applying a solution containing a reducing agent to reduce this silver salt to silver. Other means may also be readily suggested to those skilled in the art in the light of the foregoing description.

While reference has been made throughout the specification to reproducing continuous tone subject matter, and the invention is in fact primarily directed to halftone ink reproductions of such continuous tone subject matter, it is not so restricted. In reproducing line copy, e.g., printed matter, it sometimes happens that through various factors such as the "lightness" of the subject matter to be reproduced, improper exposure, etc., the resulting silver transfer image of insufficient silver density to make acceptable ink reproductions. The present invention may also be useful in obviating these problems in reproducing line copy. Accordingly, while the present invention is primarily directed to halftone reproductions of continuous tone subject matter, it is to be expressly understood that the invention is not so restricted and is applicable to lithography in general.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a process of preparing improved silver diffusion transfer printing masters for ink reproductions where a photosensitive silver halide layer is exposed through a halftone screen and developed to form an oleophilic silver transfer image at an oleophobic silver-receptive stratum, the improvement which comprises employing a silver-receptive stratum that has a substantially uniform deposit of metallic silver prior to diffusion transfer with a reflection density of from about 0.05 to 0.3, said deposit being sufficient to render wettable by greasy ink those gray image areas containing an inadequate supply of diffusion transfer silver to be so wetted, and being insufficient to render wettable by greasy ink the highlight areas of the image.

2. The process of claim 1 including the steps of wetting the silver receptive stratum containing the silver transfer image with a greasy ink and contacting this inked stratum with sheet material to provide ink reproductions of the image.

3. In a process of preparing silver diffusion transfer printing masters for ink reproductions where a photosensitive silver halide element is exposed through a halftone screen and developed in the presence of an antiadhesion reagent to form a silver transfer image at an oleophobic silver-receptive stratum having an oleophilic underlayer, the antiadhesion reagent removing from this underlayer those portions of said stratum containing sufficient transfer silver, the improvement which comprises employing a silver-receptive stratum that has a substantially uniform deposit of metallic silver prior to diffusion transfer with a reflection density of from about 0.05 to 0.3, said deposit being sufficient to render removable by the antiadhesion reagent those gray image areas containing an inadequate supply of diffusion transfer silver to so removed, and being insufficient to render removable by the antiadhesion reagent the highlight areas of the image.

4. The process of claim 3 including the steps of wetting the unremoved portions of the silver receptive stratum and its underlayer with greasy ink and contacting this inked stratum and underlayer with sheet material to provide ink reproductions of the image.

5. A method of forming a lithographic printing master by the silver diffusion transfer process comprising uniformly depositing silver on a silver-receptive stratum, after exposure through a halftone screen, in a quantity sufficient to provide a metallic silver deposit having a reflection density of from about 0.05 to about 0.3, said deposit being insufficient to render areas wettable by greasy ink; exposing a silver halide layer; developing said exposed silver halide layer and forming, as a function of said development, an imagewise distribution of soluble silver complex in undeveloped areas of the silver halide layer; transferring said imagewise distribution of soluble silver complex to said silver-receptive stratum to provide a silver transfer image, the silver transfer image including portions wettable with greasy ink, which portions would not be wettable with said ink in the absence of said first deposited silver.

6 The method as defined in claim 5 wherein said first deposited silver is provided by silver diffusion transfer processing of a uniformly but incompletely exposed silver halide layer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,639,124 Dated February 1, 1972

Inventor(s) Carole L. Groncki

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 3 change "processing" to --possessing--.
(Application page 6, line 3)

Column 3, line 50, after "description." delete "e.g.".
(Application page 7, line 22)

Column 4, line 3, change "east" to --ease--.
(Application page 8, line 19)

Column 4, line 50, change "mentioned" to --mention--.
(Application page 10, line 9)

Column 6, line 4, change "i.e." to --e.g--.
(Application page 13, line 27)

Column 8, lines40 and 41, delete "after exposure through a halftone screen"
(Amendment dated July 22, 1971, claim 20, line 4)

Column 8, line 45, after "layer" and before "developing" insert --through a halftone screen;--
(Amendment dated July 22, 1971, claim 20, line 8)

Column 8, line 49, after "stratum" and before "to" insert --containing said metallic silver--.
(Amendment dated July 22, 1971, claim 20, line 14).

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334