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[54] **PHOTOGRAPHIC PROCESS FOR PRODUCING COHERENT METALLIC IMAGE BONDED TO A ROUGHENED SUPPORT AND PRODUCTS PRODUCED THEREBY**

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[63] Continuation-in-part of Ser. No. 744,631, July 15, 1969, abandoned.

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[51] **Int. Cl.** **G03f 7/02**

[58] **Field of Search** ..... 96/86, 48, 1.5, 33, 45 PD; 101/463, 465

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[57] **ABSTRACT**

A metallic base photographic plate having images adherently and preferably conductively bonded to the metallic support is produced by contacting with metal image forming materials such as a photographic physical developer and imaging medium comprising a physically developable image. A preferred process is one utilizing a copy medium capable of being rapidly processed and having a layer of a photoconductor-binder emulson on a roughened metallic support and a physical developer capable of producing an image adherently and conductively bonded to the metallic support. The plate produced by this invention is especially useful as a printing plate, having the capability of producing high resolutions and continuous tone prints.

25 Claims, No Drawings

PHOTOGRAPHIC PROCESS FOR PRODUCING COHERENT METALLIC IMAGE BONDED TO A ROUGHENED SUPPORT AND PRODUCTS PRODUCED THEREBY

This application is a continuation-in-part application of U.S. Ser. No. 744,631, filed July 15, 1968, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to metallic base photographic plates.

2. Description of the Prior Art

Metallic base photographic plates are known in the art. Such plates usually consist of a photographic metal image on an insulating layer superposed on the base metal. Such photographic plates are proposed for use as printing plates but usually have a very limited use since the metal image which corresponds to the printed matter usually breaks down physically when used to print out multiple copies. This lack of stability of the metal image seriously limits the use of such plates for large scale printing. Attempts to improve the physical stability of the metal image have heretofore been eminently unsuccessful.

This invention relates to improved and more rapid methods of producing photographic plates having conductive metal images adherently, and in the case of metal-base media, preferably conductively, bonded to the medium support. This plate is produced by contacting an imaging medium comprising a physically developable image with metal image-forming materials such as a physical developer to produce a coherent metal image adherently bonded to said medium. Preferably this plate is prepared by exposing the selected photosensitive medium, contacting this medium with suitable image forming materials, such as a physical developer, to form a conductive metal image adherently bonded to the said medium. The copy medium useful in this invention is a medium comprising a photosensitive layer on a variety of supports and preferably on a superficially roughened metallic support or a medium comprising a physically developable image which is not adherently bonded to the support. A preferred process is one utilizing a copy medium capable of being rapidly processed and having a very thin layer of a removable photosensitive layer on a roughened metallic support with a physical developer capable of producing an image adherently bonded to the support. Rapid processing refers to contacting the copy medium with room temperature chemicals, such as silver nitrate and a reducing agent therefor to produce a conductive metal image adherently bound to the support usually in less than about 1 minute.

Once the adherent metal image is formed the developed medium can then be treated to form a printing plate. As part of such treatment, it is generally desirable to increase the oleophilic-hydrophilic differentiation between the image areas and the non-image areas of the plate. This may be done, for example, to a silver image which is deposited on an aluminum support by contacting with materials such as mercaptans which will adhere to the silver image areas making them more oleophilic, alone, or in combination with phosphoric acid which adheres to the non-image areas thereby making the non-image areas more hydrophilic. Additionally, a lithographic preparation containing a polymer such as gum arabic or carboxymethyl cellulose can be applied to improve the hydrophilic character of the non-image parts of the plate. Further, the printing life of the plate as well as the oleophilic character may be improved by coating the plate with lacquers which will adhere selectively to the image areas and not to the non-image areas. Other useful compounds for increasing the printing properties of this metal plate are disclosed in French Patent of Addition No. 77,556, herein incorporated by reference. A silver image may be made more oleophilic by amplifying in a metal ion bath which will produce a metal image more oleophilic than a silver image, e.g., a copper image.

It is preferable to remove the photosensitive layer as one of the steps of forming the printing plate although this can also be accomplished during other processing steps. Usually, this is effected by treatment with a solvent for the photosensitive layer, most commonly a solvent for the binder of the photosensitive layer. Further, the metal image of the printing plate can be amplified using amplifying systems comprising a reducible metal ion such as silver, copper or tin, together with a reducing agent therefor. This amplification is effected before or after removal of the photosensitive layer.

The photosensitive material of the present media can be any of those which permit physical development of a metal image, i.e., physically developable photosensitive materials. This type of photosensitive material is known in the art and embraces those photosensitive materials which after photoexposure are developable by what is known as physical development. Physical development is development using a solution of reducible metal ions and a reducing agent therefor which will selectively deposit metal in the photoactivated areas. In theory, the first step of such development is the formation of a latent metal image which is then intensified, or amplified, by the metal obtained by reduction of the aforesaid metal ions. The metal of the latent metal image may be the same as the so-reduced metal or different, e.g., the latent image can be silver and the so-reduced metal, copper or silver, as desired. In silver halide photography, the latent silver image forms in the silver halide emulsion and physical development is used to render the photo-image visible. Conveniently, the reducible metal ion for silver halide film is already present in the photosensitive emulsion in the form of the silver halide. However, an external source of reducible metal ion can be used in lieu thereof. Suitable photosensitive materials include silver halides, such as silver chloride or bromide; azo compounds, e.g., as described in British Specification 1,064,726, among others; photoconductors, as described in British Specification 1,043,250; and ferric compounds.

A physically-developable image can be

1. the image formed on photoexposure, e.g., the latent silver image in silver halide emulsions or the reversible latent image on a photoconductor;
2. the irreversible image formed by contacting an exposed photoconductor-bearing medium with a sensitizing metal ion, e.g., a solution of silver ion, which can lead to an invisible irreversible image or a visible metal image;
3. the latent ferrous ion image formed by photoexposure of a ferric salt-sensitized medium and then sensitized with silver ion solution to form a silver image; or

4. a conductive image produced by printing; by writing as taught in commonly owned copending U.S. Ser. No. 2,440, filed Jan. 12, 1970; by physically placing a metallic image adjacent to the support; or by diffusion transfer of metal ions as taught in U.S. Pat. No. 3,300,306.

The physically developable image may be in intimate contact with the surface of the support or may be in close proximity but slightly spaced from the support as for example where the imaging medium comprises a roughened support, a photosensitive layer containing a physically developable image, and a water permeable layer of up to a few microns thickness between the support and the photosensitive layer.

Of the photosensitive materials, especially preferred are photoconductors, particularly as described hereinafter.

The preferred copy medium of this invention comprises a metal base photographic plate with the photosensitive material preferably present in a layer of binder material. The copy medium especially preferred for use in this invention comprises a metallic base photographic plate capable of being stored in light or darkness without deterioration of its photosensitive components and capable further of being physically developed comprising a photoconductor which becomes reversibly activated upon exposure to activating radiation and is capable of causing chemical reaction in the exposed areas, this photoconductor preferably being deposited upon a superficially roughened support and the photoconductor being substantially photoconductively insulated from the metallic support. The photoconductor is preferably of a particulate nature, preferably incorporated in a photo-conductively insulating binder, and deposited as a very thin, removable layer upon the support, especially on a superficially roughened support, in such a way that the photoconductor is impregnated at least in part within the roughened portion of the support. This is readily accomplished for example by depositing a photoconductor, such as TiO_2, in a solvent-binder solution of relatively low viscosity and then coating this composition onto the roughened support. The coating composition may be allowed to dry. Such a support which has a photoconductor-binder coating will preferably have a very thin coating which is solvent permeable and will thereby allow rapid processing in the preferred developer systems.

The roughened support is a support which has been physically, chemically, or otherwise roughened in order that the metallic image forming materials are adherently bonded to the support. Physically roughened supports which are suitable for this invention are ones having grained, porous, or matted surfaces. Chemically roughened supports are ones which have been treated by suitable acids or bases, adhesive primers, adhesives, and the like to cause chemical bonding to take place between the image forming materials and the surface of the support. Additionally, additives such as cadmium and/or zinc salts may be added to the image forming materials in a manner such as described in French Patent of Addition No. 77,556 in order to improve the adhesion of the metal image to the support. Also certain alloys, such as the manganese aluminum alloy, provide good adhesion for the deposited metal image. The term "roughened supports," therefore, is intended to include a physically smooth support which by chemical or other means provides an adhesive bond with the metal image deposited thereon.

With supports comprising a plastic, especially transparent plastics, the photosensitive layer is preferably coated on a subbed plastic sheet, such as sheets of a cellulose acetate, or a polyester, especially polyethylene terephthalate, containing a layer of material which improves the adhesion of the photosensitive layer to the plastic sheet. The intermediate layer is called a subbing layer, which concept is well known to the art. Usually, subbing layers comprise materials which adhere to the plastic material and to the more hydrophilic photosensitive layer. Generally, subbing layers are comprised of gelatin, but may also comprise various latex polymers, such as various vinylidene polymers, polyvinyl formals, polyvinyl butyral and similar such materials which are known in the art. The preferred subbing layers are those which imbibe the physical developer materials, for example, gelatins.

The thickness of the photosensitive layer or the image-forming layer, and the insulating layer or subbing layer, where present, will depend upon the nature of the photosensitive material, the nature of the binder, where present, the amount of activating radiation utilized, and other like factors. However, in order to obtain an imaging medium capable of rapid processing it is preferred that these layers be relatively thin, preferably less than about 2 microns and more preferably less than about 1 micron in thickness. However, the thickness of the photosensitive layer and the insulating or subbing layer may vary. For example, in the metal support embodiment the coating may be scraped off except for the portions which are immersed in the roughened surface. The coating thickness may be varied according to the effects desired. However, most preferable is a substrate wherein the coating is less than 1 micron in thickness in order to obtain coherent metal images which are adherently bonded to the support by the rapid processing which is most desired.

When used, the amount of binder to amount of photoconductor or other photosensitive material may vary over wide ranges. Preferably, from about 1 part by weight to about 6 parts by weight of photosensitive material per part by weight of binder will be used.

In the embodiment wherein a photoconductor is immersed in the roughened surface of a metallic support the photoconductor should be insulated from the metal of the support. This insulation may be provided by the binder in which the photoconductor is dispersed, a separate insulating layer such as a silicate layer, a metal oxide of the metal of the support, or the photoconductor itself may act as an insulating layer if it is sufficiently thick.

The insulating layer is one which will photoconductively insulate the photoconductor or other photosensitive material. A photoconductive insulator as herein defined is one which will act to substantially prevent the passage to the conducting metallic support of electrons from the activated photosensitive material, e.g., a photoconductor, caused by exposure to activating radiation. This insulating layer is preferably a solvent impermeable layer at least 14 A in thickness. A preferred printing surface is an aluminum support having a barrier oxide layer of between 100 to 200 A in thickness.

The photoconductor or photocatalyst preferred in this invention are metal containing photoconductors. A

preferred group of such photosensitive materials are the inorganic materials such as compounds of a metal and a non-metallic element of Group VIA of the periodic table such as oxides, such as zinc oxide, TiO_2, zirconium dioxide, germanium dioxide, indium trioxide; metal sulfides such as cadmium sulfide (CdS), zinc sulfide (ZnS) and tin disulfide (SnS_2); metal selenides such as cadmium selenide (CdSe). Metal oxides are especially preferred photoconductors of this group. TiO_2 is a preferred metal oxide because of its unexpectedly good photosensitive properties. TiO_2 having an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature exceeding about 200°C is especially preferred, and more especially TiO_2 produced by high temperature pyrolysis of titanium halide.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide, and zinc activated zinc oxide.

While the exact mechanism by which the photoconductors of this invention work is not known, it is believed that exposure of photoconductors or photocatalysts of this invention to activating means causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conductance band of the same or at least to some similar excited state whereby the electron is loosely held, thereby changing the photoconductor from an inactive form to an active form. If the active form of the photoconductor or photocatalyst is in the presence of an electron accepting compound a transfer of electrons will take place between the photoconductor and the electron accepting compound, thereby reducing the electron accepting compound. Therefore, a simple test which may be used to determine whether or not materials have a photoconductor or photocatalytic effect is to mix the material in question with an aqueous solution of silver nitrate. Little, if any, reaction should take place in the absence of light. The mixture is then subjected to light. At the same time a control sample of an aqueous solution of silver nitrate alone is subjected to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, that material is a photoconductor or photocatalyst.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions. The more energy needed, the higher the frequency to which the photoconductor will respond. It is known to the art that it is possible to reduce the band-gap for these compounds by adding a foreign compound as an activator which either by virtue of its atomic dimensions or by possessing a particular electronic forbidden zone structure or through the presence of traps as donor levels in the intermediate zone between the valence and the conduction band stresses the electronic configuration of the photoconductive compound, thereby reducing its band-gap and thus increasing its ability to release electrons to its conduction band. Phosphors almost necessarily imply the presence of such activating substances. The effect of such impurities may be such as to confer photoconductivity upon a compound which intrinsically is non-photoconductive. On the other hand, excessive impurity content can interfere with a compound acting as a photoconductor, as above described.

The photoconductors may be sensitized to visible and other wavelengths of light by foreign ion doping, addition of fluorescent materials, and/or by means of sensitizing dyes. Bleachable dyes useful for sensitizing the photoconductors include, for example, the cyanine dyes, the dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Additional dyes which are useful for sensitizing the photoconductor are the cyanine dyes described on pages 371–429 in "The Theory of Photographic Process" by C. E. Kenneth Mees published by McMillan Company in 1952. Other useful dyes include those known to the art as triphenylmethane dyes such as crystal violet and basic Fuchsin, diphenylmethane dyes such as Auroamine O, and Xanthene dyes such as Rhodamine B.

In the embodiment of this invention wherein the conductive or latent image capable of being physically developed formed in a layer adjacent to the surface of a roughened metallic support can be physically developed to form an adherently bonded metal image in the surface of the roughened support it is not known exactly why the metal image becomes adherently bonded to the metallic support. However, it is believed that when the metallic support containing the conductive image is immersed in the physical developer, a small electrical cell may be set up between the metallic support and conductive image which causes reduction of the metal ions in the physical developer at a point on the surface of the metallic support below the conductive image, thereby depositing a metallic image in the roughened surface of the support. An alternative theory is that the physical development builds up the image until it forms in the surface of the support. It is also possible that a combination of these theories may explain this embodiment of this invention, which appears to explain the phenomenon with respect to non-metal supports, e.g., the plastic sheet media, particularly those which are subbed, e.g., with gelatin, in which the metal image appears in the subbing layer.

Irradiation sources which are useful in this invention for producing the initial latent image include any of the usual irradiation means commonly used with the selected photo-sensitive material. Thus actinic light, X-rays, or gamma rays are effective when photoconductors are used. Beams of electrons and other like particles may also be used in the place of the ordinary forms of electromagnetic radiation for forming an image. These various activating means are designated by the term "activating radiation."

In general, the media of the present invention can comprise any suitable support, for example, paper, plastics, wood, and the like, although the preferred supports are metal supports. The non-metal supports may be comprised of any suitable plastic material, which preferably include cellulose acetate and polyesters, particularly polyethylene terephthalate. The support can be in any form such as, for example, sheets, ribbons, rolls and the like. Of course, the support should be of sufficient strength and durability to satisfactorily serve as a photographic or reproduction carrier. When the support comprises a plastic, particularly a polyester, e.g., polyethylene terephthalate, it is advantageous to utilize subbing materials to ensure adhesion of the photosensitive layer to the support, as described hereinbefore.

For the preferred supports, any suitable metallic or substantially metallic backing of sufficient strength and

durability to satisfactorily serve as a reproduction carrier can be employed. The support may be in any form such as, for example, sheets, ribbons, rolls, etc. This sheet may be made of any suitable metal or their alloys, as for example the hydrophilic metals such as chromium, nickel, lead, stainless steel, magnesium, or aluminum; or the oleophilic metals such as copper or zinc. Aluminum is preferred because of its desirable physical and chemical properties, as well as its economy. A porous anodized surface is especially preferred for the aluminum support. The anodized surface may be sealed by heating. However, the unsealed surface is preferred because of the improved adhesion that can be obtained between the metal image and the aluminum support.

The support and imaging metal may be chosen so as to give a good oleophilic-hydrophilic differentiation for use in a lithographic process. Also, by special treatments or the right substrate or imaging metal this process can be used to produce a plate useful in the so-called driographic manner described in U.S. Pat. No. 3,511,178.

In all embodiments of the invention, the preferred photosensitive layer comprises the selected photosensitive material in a binder which is solvent permeable. It is often desirable with non-metal supports to utilize a coating between the roughened surface of the support and the photosensitive material, the coating being a solvent permeable binder material. With such an intermediate coating, the photosensitive material preferably in a binder is more easily coated onto the support. Better, more uniform coatings are produced when the photosensitive material in a binder is coated onto the support material, with or without the intermediate binder layer thus resulting in better quality images. In addition, by use of a solvent soluble intermediate layer such as gelatin, the problem of degradation of the photosensitive layer by contact with a metal support is overcome, the intermediate layer also serving to insulate the photosensitive material from the metal support.

A further advantage of the use of a layer of photosensitive material in a binder resides in a further preferred mode of the invention, i.e., the removal of the photosensitive layer after formation of the adherently bonded metal image.

The removal of the photosensitive layer can comprise the photosensitive material either alone or in combination with binder materials. The photosensitive material is preferably used in a binder to form the photosensitive layer on the support, the sole requirement being that the layer be removable after photoprocessing. For removal, various methods can be used including dissolution or dispersion of the photosensitive layer using suitable liquid systems, such as solvents for the binder employed. Alternatively, removal of this layer with reactive solvents such as alkali or acid can be used, e.g. aqueous sodium carbonate, dilute sodium hydroxide, dilute phosphoric acid, phosphate salts and similar reagents. Mechanical removal of the photosensitive layer can be employed, e.g. using abrasive materials. Combinations of these methods can be used, e.g., rubbing the photosensitive layer from the support in the presence of a binder solvent or dispersing agent such as water.

Thus, the binders for use in the present media can comprise any of a wide variety of materials known in the photographic art. In general, these binders are translucent or transparent so as not to interfere with transmission of light therethrough. They are desirably also solvent permeable in order to allow rapid physical development to take place. Preferred binder materials are organic materials such as natural or synthetic polymers. Examples of suitable synthetic polymers are butadiene-styrene copolymer, poly(alkyl acrylates) such as poly(methyl methacrylate), polyamides such as polyacrylamide, polyvinyl acetate, polyvinyl alcohol and polyvinylpyrrolidone. Natural polymers such as gelatin are also useful. Most preferred are those binders which are solvent soluble enough to be readily washed off after development of the image has taken place. Preferably, for convenience the binder should be removable with aqueous systems. When not so removable, then suitable solvents which will dissolve or disperse the binder should be used. Little difficulty is encountered in selecting an appropriate solvent system since a simple solubility test can be used for the said purpose by merely immersing test media consisting of the support coated with the selected binder in various solvent systems. Solubility data for most binders are usually provided in standard text or otherwise available. For example, methyl ethyl ketone, methyl isobutyl ketone, acetone, tetrahydrofuran, dioxane, and similar polymer solvents will be useful.

To obtain metal images according to this invention, the binder should not be removable by the photoprocessing conditions, i.e. the photosensitive layer should remain substantially intact during solution processing. However, if desired, binders which would dissolve in the processing solution during processing can be employed if viscous processing materials are employed, thus avoiding any substantial dissolution of the binder.

When employed as the photosensitive material, the photoconductor should be conditioned for exposure by storage in the dark from one to twenty-four hours prior to use, heating or other conditioning means known to the art. After conditioning the photoconductor is not exposed to activating radiation prior to its exposure to activating radiation for recording an image pattern.

The period of exposure to form the latent image will depend upon the intensity of the light source, particular photosensitive material, the type and amount of catalyst, if any, and like factors known to the art. In general, however, the exposure may vary from about 0.001 seconds to several minutes.

When the photosensitive material comprises a photoconductor, azo compounds, or ferric compounds, the physical developers according to this invention are intended to include those image forming systems such as described in U.S. Pat. No. 3,152,903, in British Patent Specification No. 1,043,250 and British Patent 1,064,725. These image-forming materials include preferably an oxidizing agent and a reducing agent. Such image-forming materials are also often referred to in the art as electroless plating baths. Electrolytic development such as taught in U.S. Pat. No. 3,152,969 can also be used. The oxidizing agent is generally the image-forming component of the image-forming material. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. The oxidizing and reducing agent may be combined in a single processing bath, may also be in separate bath, or one or both of these components may be incorporated in the imaging medium prior to exposure. Preferred oxidizing agents comprise the re-

ducible metal ions having at least the oxidizing power of cupric ion and include such metal ions as Ag^{+}, Hg^{+2}, Pb^{+4}, Au^{+1}, Au^{+3}, Pt^{+2}, Pt^{+4}, Ni^{+2}, Sn^{+2}, Pb^{+2}, Cu^{+1}, and Cu^{+2}.

When the photosensitive material comprises a silver halide, the physical developers can comprise a solution of an amplifying metal ion, e.g., silver, copper, tin and like ions with a reducing agent therefor, or the physical developer can comprise a silver reducing agent and a solvent for the silver halide. The silver halide solvents are well known in the photographic art and include any substance which will dissolve the unexposed silver halide of the photosensitive layer to form a solution thereof which functions as an amplifying agent for the latent image formed by the photoexposed silver halide. Commonly employed as silver halide solvents are soluble thiosulfate and thiocyanate salts, but any salt capable of dissolving silver halide, usually by complex ion formation, can be used for the same purpose as long as the complex ion formed is not of a high order of stability, i.e., not appreciably dissociated.

The reducing agent component of the said image-forming materials are inorganic compounds such as the oxalates, formates, and ethylenediaminetetraacetate complexes of metals having variable valence; and organic compounds such as dihydroxybenzenes, aminophenols, and aminoanilines. Also, polyvinylpyrrolidone, hydrazine, and ascorbic acid may be used as reducing agents in this invention. Suitable specific reducing compounds include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl glycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone, alkali and alkaline earth metal oxalates and formates.

Liquid physical developer systems are preferred for use as image-forming materials because of the excellent results obtained therewith. Any suitable solvent may be utilized. However, aqueous processing baths are preferred. While the pH of the developer is not critical, it has been found that with metal base media the best results are obtained with an acid developer, and especially one having a pH of between about 2 and 5, and especially with organic acids such as citric, gluconic, maleic, and oxalic which are metal complexing agents. A pH of about 2 to 3 is expecially preferred. It is believed that the acid functions by dissolving the oxide layer on a metal such as aluminum, therefore improving the adhesion and conductivity of the image to the metallic support.

Additionally, the image-forming materials or physical developers may contain organic acids or alkali metal salts thereof, which can react with metal ions to form complex metal anions. Further, the developers may contain other complexing agents and the like to improve image formation and other properties found to be desirable in this art.

Additional developer systems useful in this invention are those disclosed in U.S. Pat. Application Ser. No. 743,982, now abandoned, and U.S. Pat. Nos. 3,674,489 and 3,654,736 each of which are incorporated herein by reference.

The physical developers of this invention should be applied for a length of time sufficient to obtain an image adherently and, in metal base media preferably conductively, bound to the metallic support. This time period will vary according to the thickness of the photoconductor layer or thickness of the insulating layer or other separation layers, the length of exposure, nature of the binder or insulator material, ratio of photosensitive material to binder, and like factors known to the art.

A useful plating bath for amplifying a metallic image which is conductively bonded to a metal support is the one comprising a metal ion and a pickling agent for the metal of the metallic support, e.g., a solution of copper ethylene-diaminetetraacetic acid (CuEDTA) and sodium EDTA.

While this application generally describes a negative working (i.e., negative to positive or visa versa) photographic process, it should be understood that the process applies equally well to positive working processes such as described in commonly owned U.S. Pat. No. 3,718,465, U.S. 3,711,283 or U.S. Pat. No. 3,414,410.

The metal image of this invention is a lustrous, coherent metal as opposed to the particulate black or dark metal of most photographic images. Furthermore, these images are adherently bonded to the support. The type of image metal plus the bonding to the support gives the plate the capability of being used on a conventional offset lithographic printing press under ordinary operating conditions to produce at least 5,000 inked paper prints and more preferably at least 100,000 without showing any significant loss in print quality.

A process according to this invention for making ink printing plates and using these plates for printing which comprises: contacting an imaging medium comprising a physically developable image with a metal image-forming material for a period of time sufficient to produce a coherent metal image adherently bonded to the medium, contacting the surface of the imaged medium with a printing ink which selectively adheres to the image or non-image areas, and contacting the ink medium with a receptor sheet for said ink. Preferably a lithographic printing process is used by treating the surface of the imaged medium with an aqueous fountain solution, and with a printing ink having an oleophilic binding agent, whereby said ink adheres to the areas of the surface corresponding to the physically developable image, and using said inked imaging medium to print by lithography. Alternatively, a low tack ink may be used on a lithographic press without the fountain solution to print by driography. In driographic printing the non-image areas of the plate are made to reject oleo ink by, for example, coating these areas with a polysiloxane elastomeric polymer.

The invention above described is exemplified as follows:

EXAMPLE 1

A brush grained aluminum sheet material of about 0.009 inch in thickness is coated with finely divided TiO_2 dispersed in a slightly hydrolyzed polyvinyl alcohol binder. An aqueous TiO_2-polyvinyl alcohol coating formulation is applied with a 4 Mayer rod to a thickness of about 4.0×10^{-5} inches.

After drying, the printing plate thus produced is exposed to an image pattern from a light source (quartz iodide lamp) for 5 seconds duration, thereby giving an exposure of 80,000 meter candle seconds, producing a latent image on the plate medium.

The thus exposed plate is then immersed in an aqueous solution of 3N silver nitrate for 10 seconds, allowed to drain, then immersed in an aqueous developing solu-

tion having a pH of about 2.5 comprising the following:

Metol	20.0 gms.
Citric Acid	12.5 gms.
Water to a liter	

and then immersed in a sodium thiosulfate fixing bath. The coating is washed from the surface of the plate, a visible image of good density is produced on the thus treated medium. The silver image is deposited in the surface of the aluminum sheet. Attempts to erase the visible image by means of vigorous abrasion from a pencil eraser or by application of Scotch Brand Transparent Tape on the image areas and then ripping the tape off vigorously without removing the images from the plate indicates that the image is truly imbedded in the surface of the grained aluminum sheet. An ohmmeter is used to test the conductance of the image and non-image areas. Much greater conductance is shown in the image areas as compared with the non-image areas, thus showing that the image is conductively bound to the aluminum support.

The plate is then treated with the following electroless copperizing solution:

Solution I	
$Cu So_4 \cdot 5 H_2O$	40 gms.
H_2O	240 gms.
28% NH_4OH	63 mls.
Solution II	
Sodium Sulfoxylate Formaldehyde ($CH_2OHOSONa \cdot 2H_2O$)	20 gms.
H_2O	50 gms.

Just prior to use, Solutions I and II are mixed. The plate is immersed for 3–5 minutes. The results of this treatment is the copper plating of the imbedded silver image areas only. The thus copper imaged plate is then treated with a dilute solution of Phosphoric Acid (H_3PO_4), and inked with rub-up ink. The plate is now used for printing on an offset press to run off one hundred thousand (100,000) copies. Good continuous tone and half tone prints are produced. The print has a resolution of 200 lines per mm.

As an alternate procedure to contacting with the electroless copperizing solution, the silver imaged aluminum plate is contacted with a copper electroplating bath which plates out copper selectively in the silver image areas of the plate. This thus imaged plate is then used on a lithographic press for producing multiple copies.

EXAMPLE 2

A brush grained aluminum foil or sheet is coated, exposed and developed as explained in Example 1 to produce an aluminum plate with a silver image adherently bound to the grained aluminum foil. However, the plate is not treated with a copperizing solution. The deposited silver image is instead treated with the following dispersion:

2-Mercaptobenzothiazole	1.0 gms.
85% H_3PO_4	1.0 gms.
Water	80.0 gms.

The dispersion is wiped on the plate with a cotton swab. The plate is now used on an offset press. The silver image itself will now accept the greasy printing ink and the non-exposed background areas accept water.

EXAMPLE 3

An unsealed anodized aluminum sheet of about 0.009 inch in thickness is coated with finely divided TiO_2 that has been dispersed with a surface active agent and mixed with water soluble polyvinyl alcohol in an aqueous medium. The coating formulation is applied with a No. 4 Mayer rod and dried at 90°C for 10 minutes.

The thus coated sheet is exposed to actinic radiation through a negative. The sheet is then immersed in the following developer solutions:

Part I	
3N $AgNO_3$	15cc
Part II	
Metol (Eastman)	30 gms.
Citric Acid	80 gms.
H_2O	to one liter

I and II are mixed just prior to use. After the image has developed to a high density the coating is washed with water. The thus produced silver image is adherently bound to the aluminum foil. This silver image has improved printing properties as compared with the image produced in Example 1 wherein the exposed plate was contacted with the silver nitrate solution and the metol solution in separate steps. These improved printing properties were noted by the greatly improved uniformity of the images in the final copy from the printing press. The above procedure may be performed by hand or by a machine having an exposure station, a mixing means, an applicator or dip station, and a wash station in combination with a means for transporting the plate to the various stations.

The thus developed sheet is next treated with the following copperizing solution:

$CuSO_4$	.5 M
Sodium Ethylenediamine-tetraacetate(Na_4EDTA)	1 M
H_2O	to a liter

A dense copper image adherently bound to the aluminum support is produced by contact with the copperizing solution at a temperature of 55°C for 30 seconds. The ink receptivity of the resulting copper image is then improved by contacting with phosphoric acid, Bi-Kem copper activator or other solutions of this type. After treatment with activator the plate is treated with a rub-up ink and used on an offset press for producing multiple copies of high quality.

EXAMPLE 4

The procedure of Example 1 is repeated utilizing the same materials except that TiO_2 is used without a binder. However, after applying the aqueous TiO_2 slurry formulation a rubber squeegee is used to remove any coating except that which is in the grain of the roughened surface. An adherently bound silver image of good quality is produced.

EXAMPLE 5

An unsealed, porous, anodized aluminum sheet which is made of an aluminum alloy having 1.5% of manganese is coated as described in Example 1 and processed with the following viscous solutions:

Viscous Sensitizer

$AgNO_3$	255 gms.
(Hercules Powder) Klycel H.A. (thickening agent)	15
to a liter with water	

Viscous Developer

Metol	33.6 gms.
Diethylaminoethanethiol HCl	1.0 gms.
Citric Acid	5.0 gms.
Pectin	30.0 gms.

The viscous solutions are applied with a 0.0015 inch Gardner applicator. The viscous coating is removed from the surface to show a silver image which is adherently and conductively bound to the aluminum support. The thus imaged sheet is then utilized as a printing plate by processing as in Example 1.

EXAMPLE 6

A roughened aluminum sheet is coated and processed as described in Example 2 to produce adherently bound silver images on the roughened support. However, the image areas are subjected to the additional treatment:

Coat with Durolith–D–250 lacquer or any other similar lacquer which adheres to oleophilic surfaces in preference to hydrophilic surfaces.

The imaged aluminum sheet thus processed is useful as a printing plate.

A brush grained or matted steel support is used in this example in place of the aluminum support to obtain similar results.

EXAMPLE 7

A brush grained aluminum support is coated with a solvent permeable nitrocellulose coating with an aqueous slurry of titanium dioxide and allowed to dry. The thus produced plate is then exposed and processed in a physical developer comprising silver nitrate and Metol which is acidified with an aluminum complexing acid. A silver image which is adherently and conductively bound to the aluminum support is produced. The silver image is covered with the nitrocellulose coating when the TiO_2 slurry is washed off. The imaged support is useful as a nameplate.

Zinc oxide is substituted for the titanium dioxide in this Example to obtain similar results.

EXAMPLE 8

A brush grained aluminum sheet of about 0.006 inch in thickness is coated with a finely divided TiO_2 dispersed in a gelatin binder. This coating has a dry thickness of about 1.2×10^{-4} cm.

After drying the printing plate thus produced is exposed to an image pattern from an ultraviolet light source (a quartz iodide lamp) for 0.5 seconds duration, thereby giving an exposure of 8,000 meter candle seconds and producing a latent image on the copy medium.

The thus exposed copy medium is then immersed for 30 seconds in an aqueous solution of 1.0 normal silver nitrate, then immersed 30 seconds in an aqueous developing solution comprising Metol and sodium sulphite, and then immersed in a sodium thiosulfate fixing bath. A visible image of good density is produced on the thus treated copy medium.

The TiO_2-gelatin emulsion is then washed from the surface of the aluminum copy medium to disclose a silver image imbedded in the surface of the aluminum foil. Attempts to erase the visible image by means of vigorous abrasion from a pencil eraser or a similar tool indicates that the image is truly imbedded in the surface of the grained aluminum surface.

The thus produced print is suitable for use as a name plate or tag or for use as a lithographic master.

As an alternative procedure a silicate coated, brush grained aluminum support is used in this example. A silver image is produced having good adhesion to the support.

A support which is chemically grained by treating with a sodium hydroxide and then washing with phosphoric acid is used in the above example. This results in a plate having a final metal image having excellent adhesion to the aluminum support.

EXAMPLE 9

A brush grained aluminum plate with a thin photosensitive coating of TiO_2 in a water soluble poly (vinyl alcohol) binder having incorporated therein a cyanine dye sensitizer is exposed for 20 seconds through a negative with a photoflood lamp having a spectral output primarily in the visible, held 10 seconds, then immersed in 0.01 M silver nitrate for 10 seconds. The specimen is then immediately dipped into a solution which is 0.2 M in Cu EDTA and contains 2 g Metol and 7.5 g Na_2SO_3 for 30 seconds and immediately developed in Ti EDTA for 15 seconds. The photosensitive coating is then removed by washing in cold water, which also largely removes the image. However, some copper is deposited in an imagewise manner on the brush-grained surface. This image is not in contact with the aluminum as is evidenced by the fact that the copper image is not amplified when the copy medium is placed in a Cu EDTA – Na_4 EDTA plating bath.

The brush grained aluminum oxide coating is penetrated in an imagewise fashion by cycling the above specimen between the Cu EDTA bath and the Ti EDTA bath, forming a copper image cemented to the aluminum substrate. This copper image is in electrical contact with the aluminum support as is shown by the amplification of this image which occurs when the copy medium is placed in a Cu EDTA – Na_4 EDTA plating bath. This plate is then used with an oil base ink on an offset press for making multiple copies.

One particularly notable advantage of the process of this invention is that a permanent image is obtained by merely removing the photosensitive layer. This is done chemically, e.g., by washing with a solvent, or mechanically, by peeling, scraping, and the like.

EXAMPLE 10

An unsealed anodized aluminum support is coated with a solution of silver nitrate in a water permeable

binder and dried. This thus coated substrate is then coated with a slurry of TiO_2 in a water permeable binder and dried. The thus prepared copy medium is then exposed imagewise to light, contacted briefly (1–10 seconds) with a solution of Metol-phenidone acidified with citric acid 1–5 seconds, washed to remove the binder layers, and finally treated with the copperizing solution of Example 1 leaving a copperized silver image adherently and conductively bound to the aluminum support. In an alternate procedure the binder layers are peeled off to provide a binder layer containing an image on front and back in addition to the imaged aluminum support.

EXAMPLE 11

An aluminum sheet which has a thickness of 0.006 inches is etched with a sodium hydroxide solution, washed with phosphoric acid and then anodized to produce a porous aluminum oxide coating on the aluminum sheet. This sheet is then coated with titanium dioxide in an acrylate resin binder, soaked for 5 minutes in a 5% aqueous solution of cupric nitrate, and then dried. The dry sheet is exposed to a 6 watt black light "Raymaster" fluorescent bulb for 60 seconds, then immersed for 150 seconds in a copperizing solution comprising 10 ml. of 1M aqueous ascorbic acid, 10 ml. of 1M aqueous $Cu(NO_3)_2$, and 10 ml. of 0.75M triethanolamine in 50:50 H_2O—CH_3OH such as described in Belgian Patent No. 678,769. A black image having an optical density of 0.92 results which is adherently and conductively bonded to the aluminum sheet.

In an alternative method, the aluminum sheet coated with the TiO_2 coating is first exposed and then contacted with a cupric ion solution. On heating to about 75°C, the cuprous ion formed by reaction of the cupric ion and activated TiO_2 disproportionates to cupric ion and copper. The latent copper image is amplified with the above mentioned copperizing solution to produce an image of good optical density which is adherently bonded to the aluminum sheet.

EXAMPLE 12

Titanium dioxide coated anodized aluminum sheets are exposed for 3 seconds on a print box, held for 10 seconds, immersed for 10 seconds in 100 ml. of 0.0005 M $AgNO_3$ which contains 2.5 ml. 1 M Na_3NTA (sodium nitrilotriacetate) and drained for 5 seconds. The sheets are then immersed for 15 seconds in 0.3 M Cu EDTA (prepared with $CuSO_4$) and drained for 5 seconds and then developed in Ti EDTA developer for 5 seconds and finally washed, and then recycled in the Cu EDTA and Ti EDTA developer solution. The plates obtained contain images of excellent density which are adherently and conductively bound to the support.

EXAMPLE 13

One-half of the anodized surface of an anodized aluminum plate is coated with a gelatin emulsion. This plate is written on with a lead pencil and is printed on with a conductive ink. The writing and printing appears on both the gelatin coated and uncoated areas. The plate is then contacted with the copperizing solution of Example 1. An all copper image is produced which is conductively and adherently bonded to the aluminum support as shown by the adhesion tests of Example 1 and the conductivity test of Example 9.

EXAMPLE 14

An anodized aluminum support having a very thick layer of aluminum oxide is partially coated with a water permeable gelatin layer. This plate is then coated with a gelatin silver halide emulsion. The plate is then exposed through a negative and contacted with a standard silver halide Metol developer. The image produced is not adherently or conductively bound to the aluminum support in either the areas of the plate which were precoated with gelatin or in the non-precoated areas.

The above procedure is repeated with two samples. The first exposed sample is developed in a standard Metol silver halide developer, except that this developer contains 20 grams per liter of sodium thiosulfate, a silver halide solvent (See our copending U.S. Ser. No. 722,551, incorporated herein by reference for other silver halide solvents useful herein, as well as, for modifications wherein the developer is incorporated in the support prior to exposure). The second exposed sample is developed in the silver nitrateMetol-citric acid developer of Example 3. The images produced on both of these samples are adherently and conductively bound to the aluminum support in both the pre-gelatin coated and non-pre-gelatin coated areas. Both of these samples are converted to printing plates by treating with the copperizing solutions of Example 1.

EXAMPLE 15

A physically smooth aluminum foil which is an alloy of aluminum and 1.5% manganese is coated with a gelatin coating, dried, then coated with a layer of finely divided zinc oxide in a polyvinyl alcohol binder, dried and then exposed through a negative.

The thus exposed plate is then immersed in an aqueous solution of 3N silver nitrate, then contacted with an aqueous solution of 20 grams of Metal and 80 grams of citric acid per liter of water and having a pH of about 2.2, to thereby produce a silver image. The gelatin binder layer is washed from the plate to disclose a silver image adherently and conductively bound to the aluminum plate.

The following acids, which are aluminum complexing agents, are substituted in the above example for the citric acid: tartaric, maleic, gluconic, and oxalic. Similar results are obtained as when the citric acid is used. A metallic image with improved adherence to the aluminum substrate is obtained for a given processing time when the substrate is being "rapid processed."

When an unalloyed aluminum support which had a physically smooth surface was used in the above example, the image washed off the aluminum support with the rest of the gelatin coating upon washing with water. The alloyed support also showed greater photographic speed than the unalloyed sample when exposed and processed similarly.

EXAMPLE 16

An unsealed porous anodized aluminum plate coated with a water soluble, water permeable polyvinyl alcohol TiO_2 emulsion having a thickness of 1 micron. The emulsion is dye sensitized to visible light by dipping into a solution of 2-p-dimethylaminostyryl-4-methylthiazole metho chloride and then dried as disclosed in Belgian Patent No. 714,080. This thus prepared plate is then exposed by a visible light source

through a negative in projection printing procedure. The thus imaged plate is then contacted with a physical developer comprising an acidified solution of silver nitrate and Metol. After developing, the emulsion layer is washed off leaving a silver image adherently and conductively bonded to the aluminum plate. The plate is then copperized and used as a printing plate as per the procedure of Example 1.

EXAMPLE 17

An unsealed porous anodized aluminum plate coated with 4 parts by weight of titanium dioxide to 1 part by weight of a water soluble, water permeable polyvinyl alcohol to a coating thickness of 1 micron is sensitized by dipping into a solution of Neocyanine dye and then dried according to the procedure of our copending U.S. Patent Application Ser. No. 359,956, incorporated herein by reference. The plate is then exposed imagewise at a distance of 4 inches to light from a 25 watt tungsten light bulb which is filtered to remove wavelengths less than 460 millimicrons for periods of time between 3 minutes and 15 minutes to imagewise bleach the dye.

The exposed plate is then uniformly exposed to the same light source for about 5 seconds to activate the copy medium in the areas where the dye is not bleached.

The thus exposed plate is then physically developed in a solution of silver nitrate, Metol, and citric acid until the image has formed all the way through the emulsion and becomes adherently and conductively bonded to the aluminum support. The emulsion layer is then washed off to give a silver image which is a positive of the original and is adherently and conductively bonded to the support. This imaged plate is then made into a printing plate by procedures outlined in Example 1.

This procedure is repeated with the added step of immersing the dye-sensitized plate into a solution of carbon tetrabromide (2.0 g./25 ml. of petroleum ether) for 1 minute and allowing the plate to dry prior to photoexposure and the photoexposure is at 8 inches for 15 seconds with a 500 watt photoflood to bleach the dye in the image areas. The remaining processing is then followed to obtain the same results.

This use of carbon tetrabromide materially accelerates the dye-bleaching during photo-exposure. Other accelerators can be used, e.g., chloroform, bromoform, hexabromoethane, and similar such polyhalogenated compounds to obtain the same result.

EXAMPLE 18

A brush grained, silicate treated aluminum plate is coated with a layer of the following:

Ferric ammonium citrate	5 g
5% aqueous gelatin	50 ml

to which is added enough water to give 100 ml. of the mixture.

The plate is then exposed through a negative to a quartz-iodide source for 28 minutes and then is developed in a physical developer of the following composition (15 ml of solution B mixed with 300 ml of solution A).

Solution A		Solution B
Metol	30.0 g.	3 M $AgNO_3$ (aqueous)
Citric Acid	80.0 g.	
H_2O to one liter		

Total developing time is 90 seconds in the bath, after which the coating is removed under running tap water and a silver image remains on the surface of the aluminum. After treatment with a mercaptan and lacquering, the plate is suitable for use on a printing press.

When ferric oxalate or ferric ammonium oxalate is used as the light sensitive material, improved photographic images are obtained.

EXAMPLE 19

A brush grained aluminum plate is dipped in a hot chromic acid solution, washed to remove the acid, dried and coated with 4 parts by weight of titanium dioxide to 1 part by weight of water soluble, water permeable polyvinyl alcohol to a coating thickness of about 1 micron. The coated plate is then exposed with a carbon arc for one minute at a distance of 25 inches from the vacuum frame. The sheet is then immersed in the developer solution described in Example 3 wherein parts I and II are mixed just prior to use. The immersion time in the developer is 60 seconds. The developed sheet is then immediately washed with cold water to remove the photosensitive emulsion.

A series of 6 additional aluminum plates were prepared and imaged according to the above procedure except that an aluminum oxide layer was applied to the aluminum surface immediately prior to applying the photosensitive emulsion by placing the aluminum plate which has had the oxide layer removed and which has been washed in a ten percent ammonium tartrate solution and a constant current passed through the plate at different voltages. By increasing the voltage applied, the barrier oxide layer is increased. These tests indicated that a barrier oxide layer of 10 A or greater is necessary in order to obtain an imaged plate without excessive fogging. These results are tabulated as follows:

Constant Amperage × Time per Unit Area	Voltage Obtained	Approx. Thickness of Barrier Oxide Layer	Background Fog
3.0 amp-sec/ft²	at 0.55 volts	5.5 A	Very Excessive
4.5 amp-sec/ft²	at 0.79 volts	8 A	Excessive
6.0 amp-sec/ft²	at 1.00 volts	10 A	Slight
7.5 amp-sec/ft²	at 1.17 volts	12 A	None noticeable
9.0 amp-sec/ft²	at 1.31 volts	13 A	None noticeable
18.0 amp-sec/ft²	at 2.16 volts	22 A	None noticeable

When the image plates described above are prepared as printing surfaces by contacting with the dispersion described in Example 2, then contacted with a lacquer which adheres to the oleophilic image areas and then gummed and put on a printing press the copies produced from the printing plates having the background fog also show similar background fog.

EXAMPLE 20

A brush-grained, silicate coated aluminum plate is coated with the following composition:

	Molarity
2-methoxydiazobenzene sulfonate (sodium salt)	0.15
Cadmium lactate	0.1 M
Calcium lactate	0.1 M
Lactic acid (to pH = 4)	

The plate is dried for 3 minutes at 90°C and is then exposed to a quartz-iodide source at 30 inches for 222 seconds. The plate is then immersed for 20 seconds in mercurous nitrate (0.01 M) which is also 0.01 M nitric acid. After draining for 10 seconds, the plate is then immersed for 60 seconds in a development bath composed of a mixture of 15 ml. of 3N Ag NO_3 and 300 ml. of a solution of Metol (30 g./l.) and citric acid (80 g./l.) and then the coating is washed from the plate under a stream of water. A dense, coherent, lustrous silver image remained adhered to the substrate.

The silver image is then wiped with a solution of the following composition:

2-mercaptobenzthiazole	1.0 g.
phosphoric acid	5.0 g.
hexadecyltrimethylammonium bromide	0.05 g.
water	95.0 g.

While still wet, a developing lacquer is applied. After drying, the plate is used on a printing press to obtain sharp, clear copies of the original image.

EXAMPLE 21

A brush grained, silicate treated aluminum plate is coated with a composition of 5.0 g. ferric ammonium citrate and 50 g. of polyvinyl alcohol (made up to 100 cc with H_2O) using a No. 4 rod.

The dried plate is exposed for 28 minutes to a quartz-iodide lamp and developed for two minutes in the physical developer described in Example 20.

After development, the coating is wiped off with water and the plate is then treated as in Example 20 to obtain a printing plate.

EXAMPLE 22 – 27

Printing plates are prepared according to the following procedure. An aluminum plate of untreated stock is contacted with a solution of chromic acid for about one minute to remove any aluminum oxide which might have formed on the surface of the aluminum. The plate is then rinsed in distilled water, immersed in an ammonium tartrate solution having a pH of 5.5, and anodized at the appropriate amperage and voltage to obtain a pre-determined barrier oxide thickness. The thus prepared aluminum plate is then coated with particulate titanium dioxide dispersed in a polyvinyl alcohol binder to a thickness sufficient to obtain a dried coating thickness of about one-half micron.

The thus prepared photosensitive plate is exposed to an image pattern from a light source (quartz iodide lamp) for 5 seconds duration, to be given an exposure of 80,000 meter candle seconds, producing a latent image on the plate.

The thus exposed plate is then immersed in an aqueous solution of 3N silver nitrate for 10 seconds, allowed to drain, then immersed in an aqueous developing solution having a pH of about 2.5 comprising the following:

Metol	20.0 gms.
Sodium Sulfite	20.0 gms.
N-N dimethyl-paraphenylene-diamine Sulfate	1.0 gms.
Ethylene Thiourea	0.1 gms.
Polyethylene glycol tertdodecyl thioether (surfactant)	1.0 gms.
Citric Acid	12.5 gms.
Water to a liter	

and then immersed in a sodium thiosulfate fixing bath. The coating is washed from the surface of the plate, a visible image of good density is produced on the thus treated medium. The silver image deposited on the surface of the aluminum plate forms a coherent silver image which is adherently bonded to the plate. Attempts to erase the visible image by means of vigorous abrasion from a pencil eraser, or by application of Scotch Brand transparent tape on the image areas and then ripping the tape off vigorously does not remove the image from the plate. This indicates that the image is truly imbedded in the surface of the grained aluminum sheet.

The plate was then lacquered with a lithographic lacquer and put on an offset lithographic printing press and copies were run off.

The results are as follows:

Example No.	Barrier Oxide Thickness(A)	Applied Voltage (volts)	Image and Print Quality
22	0	0	No image and extremely high amount of fog.
23	7	0.5	Very weak image and extremely high amount of fog which lacquered very poorly.
24	11	0.8	Weak image, high amount of background fogging and unsatisfactory prints.
25	14	1.0	No fog-lacquered well to produce a good printing image, and relatively good quality prints.
26	30	2.2	No fog-lacquered very well to produce an excellent printing image, and very high quality prints.
27	42	3.0	No fog-lacquered very well to produce an excellent printing image and very high quality prints.

These examples indicate that a barrier oxide layer of at least about 14A is necessary to produce a good printing plate. The plates of Examples 14–16 are used in an offset lithographic press to produce thousands of copies from each plate.

In the foregoing examples utilizing titanium dioxide as the photosensitive material, it is apparent that the photoexposure and development time periods are relatively short, thus resulting in rapid processing of the photographic media. Such short periods are attributable to the speed of the titanium dioxide employed. In general, the titanium dioxide is of an average particle size of 250 millimicrons or less and preferably has been activated by heating at a temperature of from about 400° C. to about 650° C.

In all of the foregoing examples, the metal image formed on development is a continuous electrically conducted metal image, as contrasted to the normal particulate non-conductive metal image usually obtained in photographic development. The continuous metal image is formed of large contiguous particles of the metal which gives the appearance of a continuous layer. The image is characteristically lustrous, e.g., the silver images are lustrous, which is the preferred form of the metal for the contemplated uses, e.g., printing plates and electrical components, as contrasted with fine, particulate, black, non-conductive metal deposits characteristic of most photographic metal images, e.g., the black deposits of silver metal in silver halide photography, which are generally not electrically conductive.

When used in the production of printed electrical circuits, the present media after development, and preferably after removal of the photosensitive layer, can be used as is or with metal supports treated to obtain the electrical circuit by chemical removal of the metal circuit formed on the metal support. Any reagent which will attack the support but be inert to the image metal can be used to separate the metal circuit, e.g., with silver or copper images on aluminum support, alkali such as dilute sodium hydroxide, or acids, such as dilute sulfuric acid. Additional reagents for this purpose will suggest themselves to those skilled in the art. If desired, the metal circuit can first be imbedded in a suitable support before removal from the aluminum support and the circuit in suitable support is removed from the aluminum support as described.

What is claimed is:

1. Process of printing consisting essentially of:
   a. exposing a copy medium comprising a thin photosensitive layer on a roughened support to form a physically developable image in said layer;
   b. physically developing by contacting said medium with image forming materials comprising a source of metal ions and wherein the thickness of the physically developable image, the roughness of the support, the proximity of the physically developable image with respect to the surface of the support, and the length of contacting of said medium with said image forming materials being such as to thereby form a coherent metal image in said photosensitive layer which is adherently bonded and in intimate contact with said support;
   c. contacting the metal image of the surface of the metal imaged medium with printing ink which selectively adheres in an image pattern to the imaged medium; and
   d. transferring the image pattern of ink onto a receptor sheet for said ink to produce prints of the original image.

2. Process as in claim 1 wherein the printing process is carried out by lithography on a lithographic press.

3. Process as in claim 1 wherein subsequent to step (b) and prior to step (c), the step of increasing the oleophilicity of the metal image and wherein the physically developable image is at least one member selected from the group consisting of (1) the latent metal image formed on photoexposure of the photosensitive layer, (2) the irreversible image formed by contacting an exposed photoconductor layer with a sensitizing metal ion, and (3) the latent ferrous ion image formed by photoexposure of a photosensitive layer comprising a ferric salt.

4. Process as in claim 1 wherein the photoconductor comprises silver halide, titanium dioxide, or zinc oxide.

5. Process as in claim 4 wherein the photosensitive material comprises silver halide.

6. Process as in claim 2 wherein the photosensitive material of the photosensitive layer comprises silver halide having a thickness of less than about 2 microns and wherein the metal ions are silver ions.

7. Process as in claim 1 wherein the metal of the support is aluminum and wherein the insulating layer is a solvent impermeable aluminum oxide layer having a thickness of between about 100 and 200A and wherein the imaged support produced in step (b) is capable of being used on a conventional offset lighographic press under ordinary operating conditions to produce at least 100,000 inked paper prints.

8. Process of printing comprising:
   a. forming a physically developable image in a photosensitive layer of a copy medium comprising said photosensitive layer on a roughened support, the thickness of the photosensitive layer being less than about 2 microns;
   b. contacting said medium with an image forming materials comprising a source of metal ions for a period of time sufficient to produce a coherent, metal image adherently bonded to the medium and capable of being used on a conventional offset lithographic press under ordinary operating conditions to produce inked paper prints;
   c. contacting the surface of the metal imaged medium with printing ink which selectively adheres in an image pattern to the imaged medium; and
   d. transferring the image pattern of ink onto a receptor sheet for said ink to produce prints of the original image.

9. Process as in claim 8 wherein the printing process is carried out by lithography on a lithographic press.

10. Process as in claim 8 wherein subsequent to step (b) and prior to step (c) the step of increasing the oleophilicity of the metal image by contacting the metal image with a bath selected from the group consisting of a copperizing bath, a mercaptan compound-containing bath, an oleophilic lacquer solution and a bath containing a mercaptan compound and phosphoric acid.

11. Process as in claim 8 wherein the physically developable image is produced in the exposed portions of the photosensitive layer.

12. Process as in claim 8 wherein subsequent to step (b) and prior to step (c), the step of removing the photosensitive material.

13. Process as in claim 8 wherein the photoconductor comprises silver halide, titanium dioxide, or zinc oxide.

14. Process as in claim 13 wherein the photosensitive material comprises silver halide.

15. Process as in claim 8 wherein the image forming materials additionally comprise a chemical reducing agent for said metal ions.

16. Process as in claim 15 wherein the metal ions comprise silver ions.

17. Process as in claim 9 wherein the photosensitive material of the photosensitive layer comprises silver halide having a thickness of less than about 2 microns and wherein the metal ions are silver ions.

18. Process as in claim 8 wherein the support is a metal support, the surface of which has been physically roughened and contains an insulating layer between the photosensitive layer and the metal of the support.

19. Process as in claim 18 wherein the metal of the support is aluminum and wherein the insulating layer is a solvent impermeable aluminum oxide layer having a thickness of between about 100 and 200A and wherein the imaged support produced in step (b) is capable of being used on a conventional offset lithographic press under ordinary operating conditions to produce at least 100,000 inked paper prints.

20. Process as in claim 1 wherein the aluminum support is brushed grained and wherein the imaged support produced in step (e) is capable of being used on a conventional offset lithographic press under ordinary operating conditions to produce at least 100,000 inked paper prints.

21. Process as in claim 10 wherein metal image produced is silver and the material for increasing the oleophilicity of the silver image comprises a mercaptan compound and phosphoric acid.

22. Process as in claim 1 wherein the step of increasing the oleophilicity of the metal image comprises contacting with a bath selected from the group consisting of a copperizing bath, a mercaptan compound-containing bath, an oleophilic lacquer solution and a bath containing a mercaptan compound and phosphoric acid.

23. Process as in claim 1 wherein the physically developable image is produced in the exposed portions of the photosensitive layer.

24. Process as in claim 8 wherein the photosensitive material of the photosensitive layer comprises a photoconductor.

25. Process as in claim 8 wherein subsequent to step (b) and prior to step (c), the step of increasing the oleophilicity of the metal image and wherein the physically developable image is at least one member selected from the group consisting of (1) the latent metal image formed on photoexposure of the photosensitive layer, (2) the irreversible image formed by contacting an exposed photoconductor layer with a sensitizing metal ion, and (3) the latent ferrous ion image formed by photoexposure of a photosensitive layer comprising a ferric salt.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,807,304

DATED : April 30, 1974

INVENTOR(S) : Robert F. Gracia, et al

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

The term of this patent subsequent to November 27, 1990,

has been disclaimed.

Signed and Sealed this

Twenty-fourth Day of August 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks