Oct. 8, 1963 R. F. REITHEL 3,106,518

PHOTOCONDUCTOGRAPHY EMPLOYING SPONGY HYDROXIDE IMAGES

Filed June 27, 1961

Fig. 1

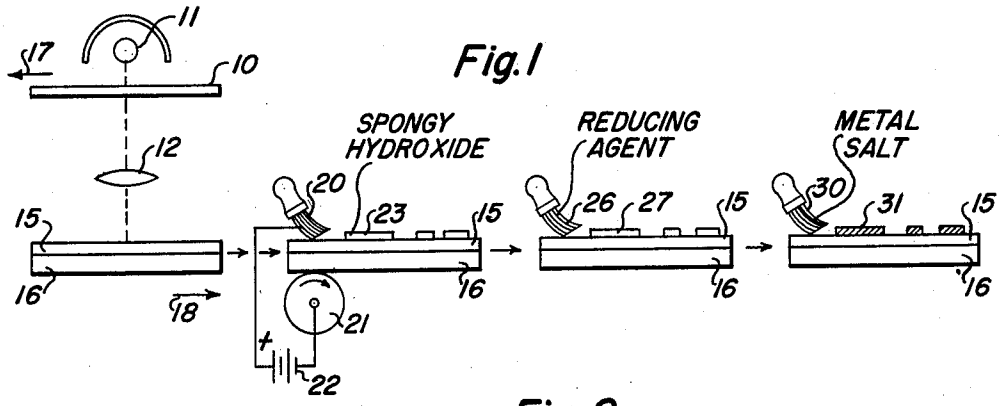


Fig. 2

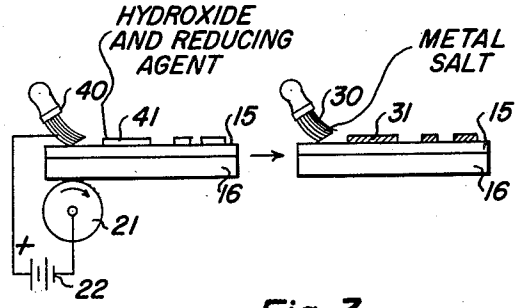


Fig. 3

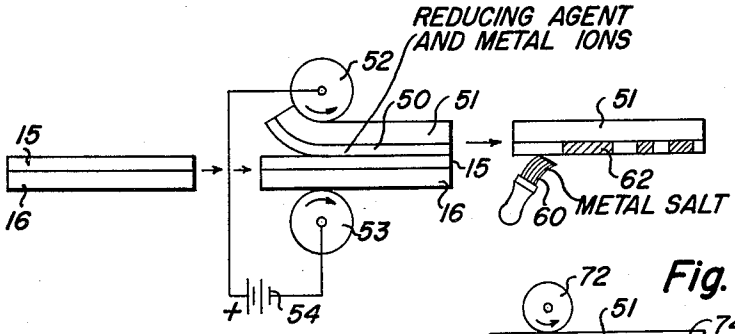
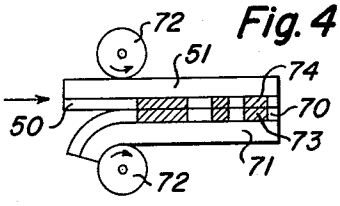


Fig. 4



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3,106,518

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10 Claims. (Cl. 204—18)

This is a continuation-in-part of U.S. Serial No. 45,943, filed July 28, 1960, and now abandoned.

This invention relates to photoconductography.

Photoconductography forms a complete image at one time or at least a non-uniform part of an image as distinguished from facsimile which at any one time produces only a uniform dot. The present invention would be useful with facsimile but finds its greatest utility in photoconductography.

Cross reference is made to the following series of applications filed July 28, 1960, concurrently with the application of which this is a continuation-in-part.

Serial No. 45,940, John W. Castle, Jr., "Photoconductography Employing Reducing Agents."

Serial No. 45,941, Raymond F. Reithel, "Photoconductolithography Employing Nickel Salts," now abandoned, and continuation-in-part Serial No. 120,863, filed June 7, 1961.

Serial No. 45,942, Raymond F. Reithel, "Photoconductolithography Employing Magnesium Salts," now U.S. Patent 3,053,179.

Serial No. 45,944, Raymond F. Reithel, "Method for Making Transfer Prints Using a Photoconductographic Process."

Serial No. 45,945, Raymond F. Reithel, "Photoconductography Employing Manganese Compounds."

Serial No. 45,946, Raymond F. Reithel, "Photoconductography Employing Molybdenum or Ferrous Oxide," now abandoned, and continuation-in-part Serial No. 120,036, filed June 27, 1961.

Serial No. 45,947, Raymond F. Reithel, "Photoconductography Employing Cobaltous or Nickelous Hydroxide," now abandoned, and continuation-in-part Serial No. 120,037, filed June 27, 1961, now U. S. Patent 3,057,788.

Serial No. 45,948, Donald R. Eastman, "Electrophotolithography."

Serial No. 45,949, Donald R. Eastman, "Photoconductolithography Employing Hydrophobic Images."

Serial No. 45,950, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Electrolytic Images to Harden or Soften Films."

Serial No. 45,951, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Absorbed Metal Ions," now abandoned, and continuation-in-part Serial No. 120,038, filed June 27, 1961.

Serial No. 45,952, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Spongy Images Containing Gelatin Hardeners."

Serial No. 45,953, John J. Sagura, "Photoconductography Employing Alkaline Dye Formation," now U.S. Patent 3,057,787.

Serial No. 45,954, John J. Sagura and James A. Van Allan, "Photoconductography Employing Quaternary Salts."

Serial No. 45,955, Frang Urbach and Nelson R. Nail, "Uniform Photoconductographic Recording on Flexible Sheets."

Serial No. 45,956, Franz Urbach and Nelson R. Nail, "High Contrast Photoconductographic Recording.'

Serial No. 45,957, Nicholas L. Weeks, "Photoconductography Involving Transfer of Gelatin."

Serial No. 45,958, Donald R. Eastman, "Photoconductolithography Employing Rubeanates."

Serial No. 45,959, Donald R. Eastman and Raymond F. Reithel, "Electrolytic Recording With Organic Polymers."

Serial No. 46,034, Franz Urbach and Donald Pearlman, "Electrolytic Recording."

Electrolytic facsimile systems are well known. Electrolytic photoconductography is also known and is described in detail in British 188,030 von Bronk and British 464,112 Goldmann, modifications being described in British 789,309 Berchtold and Belgium 561,403 Johnson et al.

The present invention is related particularly to those photoconductographic processes in which the final print is formed directly on the photoconductive layer used in the process, but some embodiments produce the print on a separate sheet.

The present invention provides great versatility in photoconductography, possibly greater than that available in all prior forms thereof combined. The versatility is due to the fact that, by the present invention, innumerable different recording reactions (different chemical reactions used for recording) are made available for and applicable to photoconductography. Thus, in each case, the peculiar advantages of each such reaction constitute objects of the present invention.

As will be apparent from the description of the various embodiments of the present invention, these objects include such features as high photo speed, uniformity of reproduction, proper tonal range and distribution, choice of color, low cost, good keeping qualities and non-toxicity of the materials used. For example the uniformity can be so easily controlled in certain embodiments of this invention that excellent continuous tone images are obtained. However, these embodiments and all others are applicable to line copy processes.

The invention consists of depositing electrolytically by photoconductographic methods, a spongy image and by absorbing into this image a chemical reagent which is thus distributed imagewise. The term "spongy" refers to the character of the image which permits it to absorb or adsorb a reagent such as a reducing agent, oxidizing agent, alkaline or acid solution etc. Then, according to the invention, a second chemical reagent is brought into contact with the imagewise distributed first reagent to produce either a visible image directly or an image in terms of softness or solubility of a gelatin or a polymer or in terms of hydrophobicity or even in terms of the production of an intermediate which is then used in a more complex process. In all embodiments of the invention, the spongy image provides the environment or container in or at which the chemical reaction takes place. The importance of this chemical reaction feature in a spongy image is almost boundless.

The first chemical reagent is, in some embodiments of the invention, applied directly from the electrolyte; in others it is applied subsequent to the formation of the image. Of course this first reagent must be compatible with the spongy image and with the surface on which the spongy image is deposited. For example it must not dissolve the image. The second reagent may be applied as a solution directly to the spongy image. In other embodiments the second reagent is coated on a separate sheet, for example in the form of a solution in a web, or gelatin layer. Whether the second reagent is simply a liquid applied to the image or is in a separate sheet, the final image resulting from the reaction of the two reagents may be on the photoconductive surface where the spongy image was located, may be on the separate sheet or may even be transferred to a third receiving sheet.

Many of the cofiled applications listed above disclose examples of the present invention, combined in each case with the invention of that particular application. Such examples as well as those given below are illustrative of the great variety of forms which the invention may take.

In one preferred form of the invention the photoconductographic image is a porous or spongy image of metal hydroxide such as the alkaline earth hydroxides and this spongy-like structure is used to absorb a reducing agent, which eventually reduces a metal salt to a metal image.

In a somewhat different embodiment the same metal or alkaline earth hydroxide image is formed partly on, or is transferred to, a gelatin or similar water permeable layer containing a reducing agent which is active only when alkaline and the hydroxide image provides the necessary alkalinity. Photographic developers have this latter property and such developers are quite useful in this particular embodiment of the present invention. The spongy feature of the image allows the developer to penetrate the image and the alkaline character renders the developer active, the cofiled application by Sagura on alkaline images uses the high pH for dye formation.

According to the present invention a photoconductographic process involves electrolytic deposition on or at the surface of an exposed photoconductive layer of a hydroxide image from an electrolyte containing ions selected from the group consisting of aluminum, magnesium, cobalt, iron, nickel, and chromium. These particular hydroxides are insoluble or have relatively low solubility so that they can be deposited electrolytically. The deposits formed are porous as well as alkaline. According to the invention a chemical reagent (e.g. a reducing agent) is applied to the hydroxide image and is absorbed by this image. A solution of a second reagent which reacts with the first (e.g. a solution of metal salt which is reduced by the reducing agent, for example, a silver salt which is reduced by a photographic developer) is applied to the spongy hydroxide containing the first reagent. In my cofiled application with Eastman entitled "Photoconductography Employing Spongy Images Containing Gelatin Hardeners" the examples given are also examples of one species of the present invention.

In the simplest embodiment of the invention, the hydroxide image is deposited directly on the photoconductive layer and simultaneously or later treated with an agent which is absorbed only by the hydroxide image and not by the photoconductive layer itself which tends to be hydrophobic. The image is then washed or brushed with a solution of the second agent for example, thus forming the final print on the photoconductive layer.

In an alternative embodiment the exposed photoconductive layer (during exposure or, if the photoconductive layer is of the type which retains its conductivity image, immediately following exposure) is placed in contact with a gelatin or other water permeable layer containing the metal or alkaline earth ions listed above and also containing a reducing agent which is not active at the low pH of the salt solution but which becomes reducing when alkaline. Direct electric current is then passed through the water permeable layer with the photoconductive layer as cathode so that hydroxide of the metal or alkaline earth ion is deposited at the surface of the photoconductive layer. At least some of this hydroxide is formed or transfers with the water-permeable layer when the layers are separated. The hydroxide ion is alkaline and hence the layer is reducing in the areas of the hydroxide image. This image may then be swabbed with the solution of a reducible metal salt such as silver lactate or silver nitrate or may be pressed against a surface which has been treated with a solution of such a salt, so that the metal salt is reduced to metal forming the image on the water permeable sheet or on the separate sheet, as the case may be.

Advantages and various features of the invention will be fully understood from the following description when read in connection with the accompanying drawing in which:

FIG. 1 is a flow chart schematically illustrating a preferred embodiment of the invention.

FIG. 2 similarly illustrates the arrangement for combining two of the steps of FIG. 1.

FIG. 3 similarly illustrates an alternative embodiment of the invention and

FIG. 4 illustrates an alternative for one of the steps of the process illustrated in FIG. 3.

In FIG. 1 a negative transparency **10** illuminated by a lamp **11** is focused on a photoconductive layer **15**, for example zinc oxide in suitable resin, carried on a support **16**. The transparency **10** and the photoconductive layer **15** move synchronously as indicated by arrows **17** and **18**. Immediately following exposure of the layer **15**, it is subjected to an electrolyte bath by brushing the surface with a brush **20** containing a solution of salts of alkaline earths or certain metals capable of forming an insoluble porous hydroxide upon cathodic deposition on the photoconductive layer **15**. The necessary D.C. current is provided by the brush **20** and a backing roller **21** from a source of potential indicated schematically at **22**. The hydroxide is deposited as shown at **23** on the areas of the photoconducting layer **15** which have been rendered photoconducting by exposure to light from the transparency **10**. A gelatin or other water permeable layer may, of course, be used in place of the brush **20** to apply the electrolyte.

The hydroxide image **23** is porous or sponge-like so that it behaves in a hydrophilic manner when swabbed by a brush **26** containing a reducing agent. Thus the image **27** is made up of the hydroxide and absorbed reducing agent. A solution of a metal salt such as silver nitrate in a third brush **30** applied to the reducing image **27** causes the metal itself to be deposited forming a dark image **31** which in this case constitutes the final print image.

In FIG. 2 the electrolyte in the brush **40** contains both magnesium ions which deposit as magnesium hydroxide and a reducing agent which is absorbed by the image **41** as it is deposited. Then, as in FIG. 1 it is treated with a reducible metal salt in solution in the brush **30** to form the visible image **31**.

In FIG. 3 the exposed photoconductive layer **15** is pressed into contact with a gelatin layer **50** carried on a suitable conducting support **51** and the sandwich is passed between electrode rollers **52** and **53** provided with a potential difference from a source **54**. The gelatin layer **50** has been previously soaked in a solution of a salt of one of the alkaline earths or metals mentioned above so that it contains ions of this alkaline earth or metal and is acid or neutral in pH. It also contains a reducing agent such as a photographic developer which, due to the acid or neutral condition is not active. The electrolyte action of the current passing between the electrodes **52** and **53** deposits at the interface between the layer **15** and the layer **50** a hydroxide of the ion just mentioned and this hydroxide is spongy and alkaline. At least part of the hydroxide adheres to the layer **50** as it is removed from the photoconductive layer **15**. Swabbing the layer **50** with a brush **60** containing silver nitrate or similar reducible salt causes silver, or other metal, to be deposited in the areas of the hydroxide and reducing agent to form the dark image **62** on the gelatin layer. The lateral inversion of the image is provided for by projecting a reversed image of the photoconductive layer **15** at the time of exposure. The image **62** is permanent, but the excess reducing agent in the layer **50** is preferably removed, by washing, to prevent staining of the final image.

A slightly different arrangement is shown in FIG. 4 wherein the layer **50** containing the hydroxide image and the reducing agent which is activated in the region of the hydroxide image, is pressed into contact with receiving sheet **71** whose surface **70** has been treated with a solution of a reducible metal salt, by passing between rollers

72. The image areas reduce the metal salt in the layer 70 to a metal to form an image 73 and the final print is preferable fixed to remove excess metal salt. Some of the image transfers as shown at 74 to the layer 50.

As examples of my invention, one can use any of the hydroxides mentioned above and any of the photographic reducing agents such as the whole family of substances discussed on page 547 of "The Theory of the Photographic Process," by C. E. Mees, and various inorganic reducing compounds such as ferrous sulfate, and stannous sulfite have proven to be satisfactory.

Example 1

A dye-sensitized zinc oxide layer on a conducting support was exposed imagewise to 400 ft. candle intensity for 5 seconds. This intensity is the highest occuring in the image on the zinc oxide. The conducting image was developed electrolytically using a viscose sponge brush electrode, held at 80-volt potential, positive with respect to the zinc oxide layer, and a solution consisting of 0.8% magnesium sulfate plus 0.2% hydroquinone at an initial pH of 8.0. Development was done with 10 strokes of a brush electrode at the rate of one stroke per second across the zinc oxide surface. A colorless magnesium hydroxide image formed, containing absorbed hydroquinone proportionate to the amount of image, which in turn was proportional to the exposure. This image was chemically developed by bathing with a 5% silver nitrate solution to produce a chemical deposit of metallic silver which is directly related to the amount of magnesium hydroxide and reducing agent deposited on the zinc oxide surface.

Example 2

As an alternative example of this invention, the magnesium hydroxide was first deposited electrolytically alone, followed by bathing the image with a solution of hydroquinone. The surface was rinsed for a short time and the hydroxide image material, containing adsorbed hydroquinone, was bathed with a 5% solution of silver nitrate to produce the visible image by chemical reduction of silver ions.

Example 3

A dye-sensitized zinc oxide layer on a conducting support was exposed imagewise to 400 ft. candle intensity for 5 seconds. The conducting image was developed electrolytically using a viscose sponge brush electrode, held at 80-volt potential, positive with respect to the zinc oxide layer, and a solution consisting of 0.4% nickelous chloride plus 0.1% 2,4,6-triaminophenol. Development was done with 10 strokes of the brush electrode at the rate of one stroke per second across the zinc oxide surface. The resulting faintly visible nickelous hydroxide or hydrated oxide, containing adsorbed 2,4,6-triaminophenol (a reducing agent) was then chemically developed to a dark, visible metallic silver (or gold) image by bathing the hydroxide image with a 5% solution of silver nitrate or gold chloride.

Example 4

A dye-sensitized zinc oxide layer on conducting support was exposed imagewise to 400 ft. candle intensity for 10 seconds. The conducting image was developed electrolytically using a viscose sponge brush electrode, held at 80-volt potential, positive with respect to the zinc oxide layer, and a solution consisting of 0.8% magnesium sulfate plus 0.2% ferrous sulfate. Development was done with 10 strokes of the brush electrode at the rate of one stroke per second across the zinc oxide surface. The resulting, faintly visible magnesium hydroxide image, containing adsorbed ferrous sulfate and possibly some ferrous hydroxide was then developed chemically to a dark visible metallic image with a 5% solution of silver nitrate.

Example 5

A dye sensitized zinc oxide layer was exposed for 10 seconds through a 0.3 density increment step-wedge to 400 ft. candle tungsten illumination. The resulting conducting image was developed electrolytically using a solution consisting of 0.4% by weight of nickelous chloride hexahydrate and 0.1% of 2,5-dihydroxyphenyl-isothiouronium chloride, contained in a viscose sponge brush electrode, held at 80 volts potential postive with respect to the zinc oxide layer, and using ten-strokes development. The excess developer was removed from the surface of the zinc oxide layer with an absorbent tissue (alternatively, a blotter or squeegee may be used). The resulting, faintly visible, electrolytically formed nickelous hydroxide (or hydrous oxide) material to which was adsorbed the reducing material 2,5-dihydroxyphenyl-isothioronium chloride, was made usefully visible by bathing the image material with a 5% silver nitrate solution. A dark brown image of reduced silver was formed in the body of the hydroxide material. The density achieved was in proportion to the amount of hydroxide material deposited. The reflection density of this material at the highest exposure was 1.04 above base density. The gamma was 0.57. This image-forming material is therefore much more conducive to producing good continuous-tone prints from a negative than that of an electrolytic single-step developer like silver nitrate-thiourea which produces maximum density of 0.55 and a gamma of 0.30 when used as a developer for this zinc oxide layer.

Example 6

A dye-sensitized zinc oxide layer was exposed for 5 seconds through a 0.3 density increment step-wedge to 400 ft. candle tungsten illumination. The resulting conducting image was developed electrolytically using a solution consisting of 0.4% by weight of nickelous chloride hexahydrate and 0.1% by weight of sodium rhodizonate contained in a viscose sponge brush electrode held at 80 volts potential, positive with respect to the zinc oxide layer, and using ten-strokes development. The resulting yellowish image material was bathed with a 5% solution of silver nitrate which was reduced chemically in the body of the hydroxide material by the adsorbed sodium rhodizonate to form a dark-brown useful image.

Example 7

The above Example 6 was repeated using 0.8% magnesium sulfate heptahydrate and 0.2% sodium rhodizonate in place of the 0.4% nickelous chloride hexahydrate plus 0.1% sodium rhodizonate.

Example 8

The process of Example 6 was repeated except that 0.4% ferrous sulfate heptahydrate plus 0.1% sodium rhodizonate was substituted for the 0.4% nickelous chloride hexahydrate plus 0.1% sodium rhodizonate.

In Examples 6, 7 and 8 it is believed that the hydroxide is electrolytically deposited and the sodium rhodizonate is absorbed or adsorbed substantially unchanged. However, when the iron or nicket salt is a chloride, a complex ferrous or nickelous rhodizonate salt is apparently deposited which is also spongy. It may be that momentarily the hydroxide still is deposited but it does not persist. The spongy deposit is hydrophilic and the plate can be used for litho printing as in some of the cofiled applications mentioned above. Examples of this variation are as follows:

Example 9

A sheet of photoconductive material was exposed for 10 seconds to 15 ft. candle tungsten radiation incident upon a high contrast positive transparency in contact with the photoconductive surface and then electrolytically developed with an aqueous solution containing 0.4 percent ferrous chloride tetrahydrate and 0.1 percent sodium

rhodizonate. The print surface was then rinsed, and "wetted-out" with 1:7 Repelex and mounted on a No. 1250 multilith press using ML–70 ink and 1:7 Repelex fountain solution. Approximately 100 prints were obtained from this master. This spongy image is also directly applicable as an environment for a chemical reaction in accordance with the present invention.

Example 10

A piece of photoconductive material was exposed in the same way as in Example 6 but electrolytic development was carried out with an aqueous solution containing 0.4 percent, by weight, nickel chloride hexahydrate and 0.05 percent by weight, sodium rhodizonate. The surface of the print was rinsed, "wetted-out," and inked as in Example 9. The areas exposed for 40 ft. candle seconds or less, held the ink. This developer provides an improvement in that the exposure scale, between ink-repellency and ink receptivity, is much shorter. Again, the image is spongy and hence useful in the present invention.

Example 11

Another piece of photoconductive material was exposed for 10 seconds to 15 ft. candle tungsten radiation incident upon a high contrast positive transparency in contact with the photoconductive surface and then electrolytically developed as in the preceding Example 10 to form a spongy image useful for chemical reaction or for litho. In the latter case the print surface was rinsed with water, "wetted-out" with 1:7 Repelex and run on a No. 1250 multilith press with the same ink, and fountain solution described in Example 10. From this master, 150 prints were produced.

In addition to the examples in the cofiled Eastman and Reithel case mentioned specifically above and entitled "Photoconductography Employing Spongy Images Containing Gelatin Hardeners," the following cofiled cases also employ spongy images.

FIG. 9 of the Castle "Photoconductography Employing Reducing Agents."

All examples of Eastman and Reithen "Photoconductography Employing Absorbed Metal Ions."

Examples 3, 8, 10, 11, 12 of my application on manganese compounds.

Examples 3, 4, 5 of my application on molybdenum and iron hydroxide.

All of the examples in my two applications on photoconductolithography (with magnesium salts and nickel salts respectively).

All of the examples in Eastman "Photoconductolithography Employing Rubeanates."

In the electrolytic processes described in this and the various copending applications referred to above there are in general no critical or special limits on the potential applied or the concentration of the salts in the electrolyte. Of course the potential cannot be so high that it causes electrical breakdown of the photoconductive layer and cannot be so low that there is no appreciable electrolytic effect within a reasonable time. Similarly the concentration of the salt in the electrolyte cannot be above saturation or cannot be so low that there is no appreciable deposit during a reasonable period of electrolytic action.

However, in the case of nickel salts when the hydroxide of the metal is to be deposited, there is a minimum voltage (about 30 volts) and a maximum concentration (about 3%), since at lower voltages or at higher conconcentrations the metal itself, without a useful amount of the hydroxide, tends to deposit. All of the examples involving nickel given in the present series of applications do have concentrations below 3% and voltages above 30 volts so that useful amounts of hydroxide are deposited. Whether metal is also deposited is of little concern.

Nickel hydroxide is much more hydrophilic than nickel metal and is more absorbent (spongy) than nickel itself. Also nickel metal images do not have satisfactory optical density whereas the deposit of nickelous hydroxide and conversion to nickelic oxide does give a high density. These various effects are involved in different applications of this present series. Also any concentration above 3% not only gives adverse effects, but adds to the cost of whichever process is involved.

As with other materials, the upper limit on the voltage is that imposed by electrical breakdown and the lower limit on concentration of nickel salts is merely that amount which gives an appreciable deposit in a reasonable time under the voltage available. This lower limit is obviously not critical.

Cobalt and iron salts behave somewhat like the nickel salts. At higher concentrations and lower voltages, the ratio of metal (or at least of a metallic like deposit which appears) to hydroxide increases. Cobalt hydroxide images appear light blue and ferrous hydroxide images appear olive green. When the process involves producing cobaltic oxide (which has a good density compared to a cobalt metal image) the concentration should be below 3% and the voltage above 30 v. (as in the case of nickel). Iron is not used in such processes since ferric oxide and hydroxide are light colored. When the process involves sponginess or physical absorption by the image, both iron and cobalt must again be used in concentrations below 3% and at voltages above 30 v. since the hydroxide images are much more absorptive than the metal images. When the process involves the hydrophilicity of the image, 30 v. is still the lower useful limit and the preferred concentrations are still below 3% although higher concentrations of iron salts and particularly of cobalt salts still give useful results because the metal images themselves have considerable hydrophilicity although not nearly as good as that of the corresponding hydroxides. Finally, when the process involves reduction (nickel hydroxide images by themselves are never used in reducing processes) the limits on concentration and voltages are only the general ones (i.e. up to saturation and between the voltage which gives an appreciable deposit in a reasonable time and the voltages which cause breakdown) because the metal image itself is reducing for both cobalt and iron.

Having thus described several examples of my invention, it is pointed out that the invention is not limited thereto, but is of the scope of the appended claims.

I claim:

1. In a photoconductographic process in which variations in electrical conductivity have been produced in an image pattern across a photoconductive electrode layer, the steps comprising electrolytically cathodically depositing on the electrode layer, a spongy metallic compound image distributed in accordance with the variations of electrical conductivity; applying to the spongy image a liquid reagent which is substantially chemically unreactive with the spongy image and the electrode layer, such that the spongy image absorbs an amount of the liquid reagent distributed in accordance with the distribution of the spongy image; applying a second reagent substantially chemically unreactive with the spongy image and chemically reactive with the liquid reagent in the environment of the spongy image, and reacting the second reagent with the amount of the liquid reagent absorbed in the distributed spongy image to form a reaction product having an imagewise distribution according to the distribution of the spongy image.

2. The process according to claim 1 in which said electrolytically depositing is from an electrolyte containing ions selected from the group consisting of aluminum, magnesium, cobalt, iron, nickel, and chromium and the resulting spongy image is the hydroxide of said ions.

3. The process according to claim 1 in which said liquid reagent is a solution of a reducing agent.

4. The process according to claim 1 in which said electrolytically depositing is from an electrolyte containing sodium rhodizonate and a salt selected from the group consisting of ferrous chloride and nickel chloride and the resulting spongy image is a spongy rhodizonate of the metal.

5. The process according to claim 1 in which the electrolyte for said depositing contains said liquid reagent whereby the latter is applied to the spongy image as the spongy image is deposited.

6. The process according to claim 1 in which the second reagent is on the surface of a receiving sheet which is brought into contact with the spongy image to form the reacting product image on said receiving sheet.

7. In a photoconductographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer by imagewise exposure to light, the steps comprising placing the layer in contact with an aqueous electrolyte solution containing ions selected from the group consisting of aluminum, magnesium, cobalt, iron, nickel, and chromium, passing direct electric current through the solution with the layer as cathode to deposit hydroxide of said ions at the layer in accordance with said pattern, applying to, for absorption by, the hydroxide image a reducing agent and then applying to the image a solution of a metal salt which is reduced by said reducing agent.

8. In a photoconductographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer by imagewise exposure to light, the steps comprising placing the layer in contact with a water permeable layer wet with an aqueous electrolyte solution containing ions selected from the group consisting of aluminum, magnesium, cobalt, iron, nickel,

and chromium and also containing an agent which is reducing when at the pH of hydroxides of said ions but not reducing at the lower pH of said electrolyte, passing direct current through the water permeable layer with the photoconductive layer as cathode to deposit hydroxide of said ions at the interface between the layers in accordance with said pattern, separating the water permeable layer with at least part of the hydroxide image thereon from the photoconductive layer, said agent being reducing at said image and bringing said image into contact with a reducible metal salt to reduce it to a metal image.

9. The process according to claim 8 in which the reducible metal salt is on a separate sheet.

10. In a photoconductographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer by imagewise exposure to light, the steps comprising placing the layer in contact with an aqueous electrolyte solution containing ions selected from the group consisting of aluminum, magnesium, cobalt, iron, nickel, and chromium, passing direct electric current through the solution with the layer as cathode to deposit hydroxide of said ions at the layer in accordance with said pattern, applying to the hydroxide image an agent which is reducing when so applied and bringing said image of hydroxide and reducing agent into contact with a reducible metal salt to reduce it to a metal image.

References Cited in the file of this patent

UNITED STATES PATENTS

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3,010,883	Johnson et al.	Nov. 28, 1961

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,106,518 October 8, 1963

Raymond F. Reithel

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 65, for "Frang" read -- Franz --; column 7, line 41, for "Reithen" read -- Reithel --; column 9, line 14, for "reacting" read -- reaction --.

Signed and sealed this 5th day of May 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents