

Jan. 4, 1966

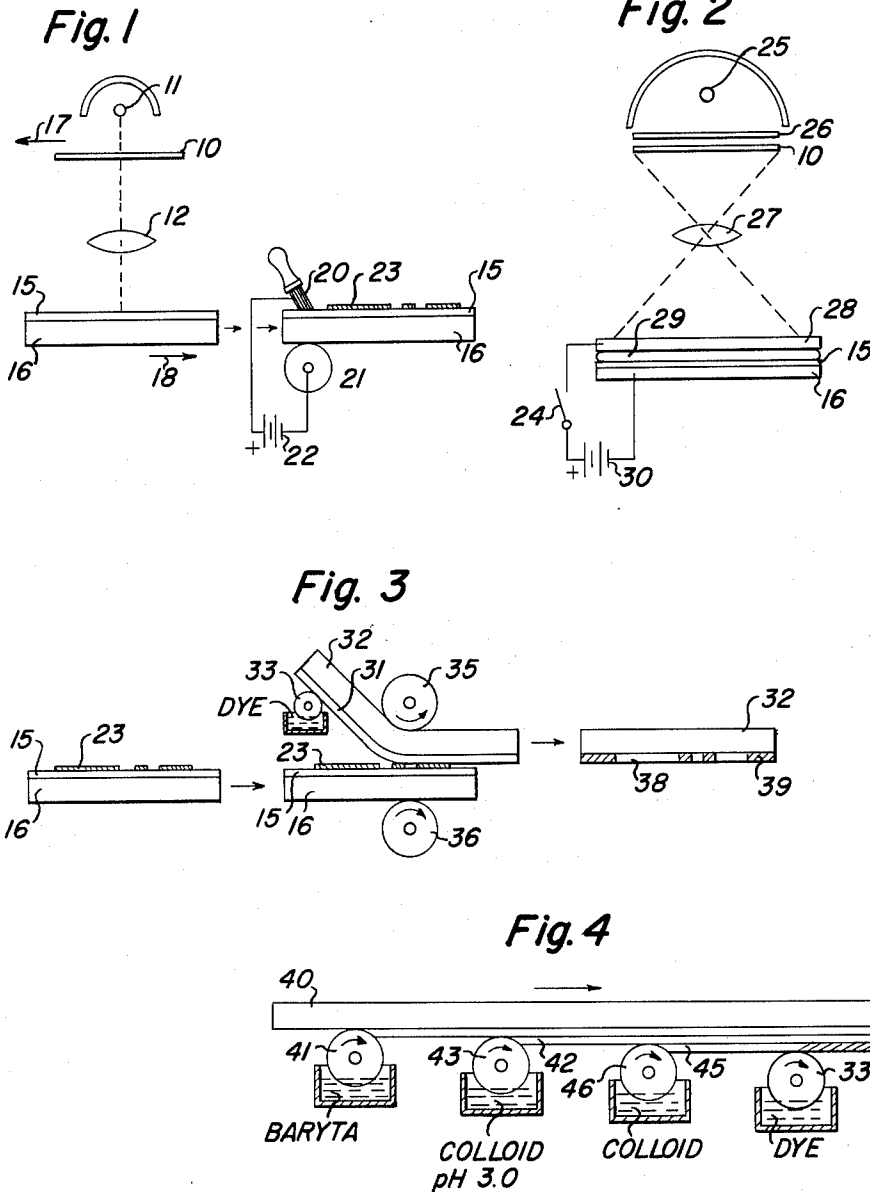
J. W. CASTLE, JR

3,227,076

PHOTOCONDUCTOGRAPHY EMPLOYING REDUCING AGENTS

Filed July 28, 1960

2 Sheets-Sheet 1



JOHN W. CASTLE JR.
INVENTOR.

BY *R. Frank Smith*
F. M. Emerson Holmes
ATTORNEYS

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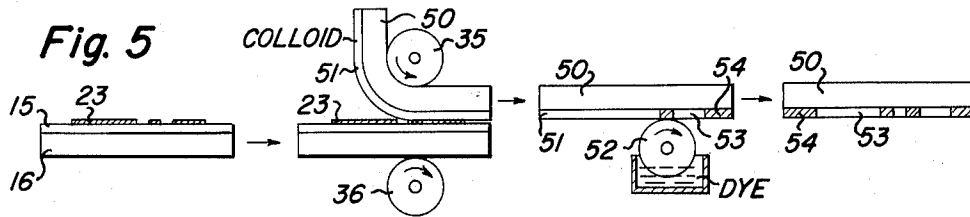
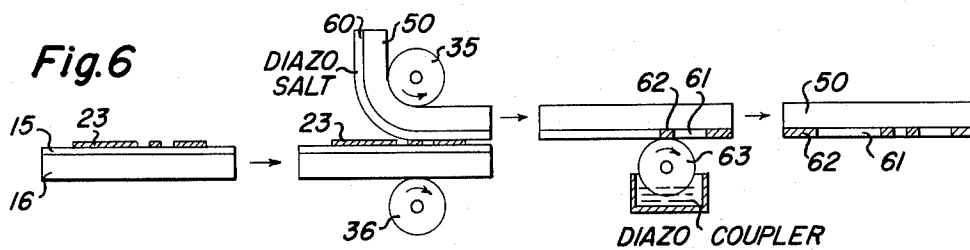
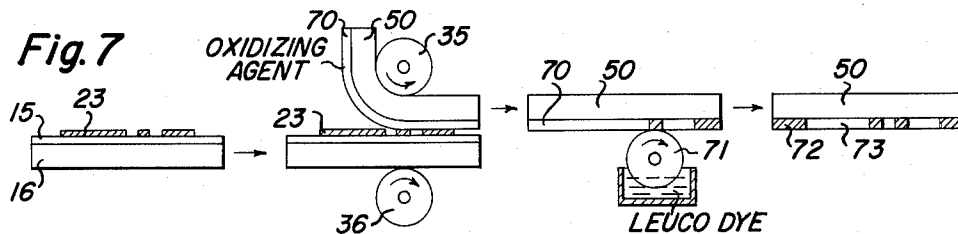
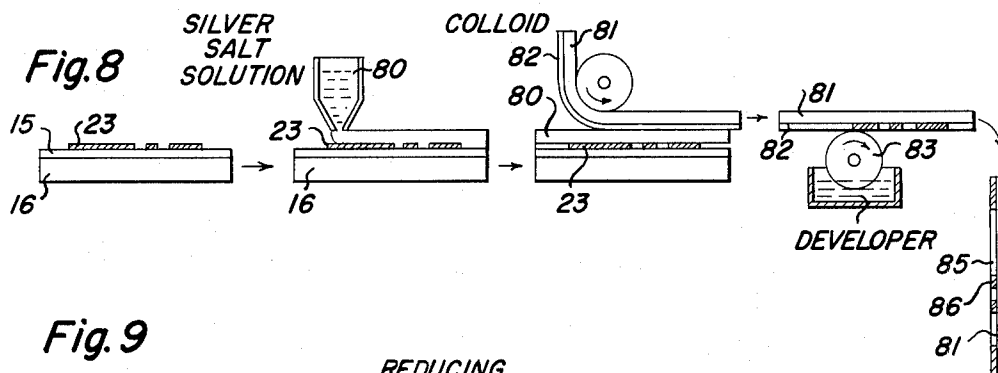
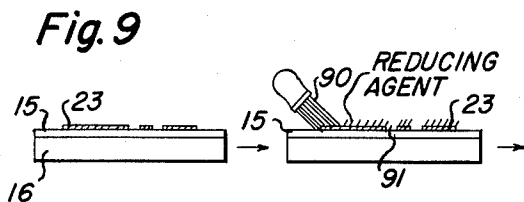
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2 Sheets-Sheet 2



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INVENTOR.

BY *R. Frank Smith*
F. M. Emerson Holmes

ATTORNEYS

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PHOTOCONDUCTOGRAPHY EMPLOYING REDUCING AGENTS

John W. Castle, Jr., Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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10 Claims. (Cl. 101-149.4)

The present invention relates to electrolytic recording and particularly 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 moment produces only a uniform dot. The present invention relates particularly to that form of photoconductography in which the final image is produced on a sheet different from and eventually separated from, the photoconductive layer.

Cross reference is made to the following series of co-filed applications:

Serial No. 45,941, now abandoned, Raymond F. Reithel, "Photoconductolithography Employing Nickel Salts," continuation-in-part Serial No. 120,863, now U.S. Patent No. 3,106,157, patented Oct. 8, 1963, filed June 7, 1961.

Serial No. 45,942, now U.S. Patent No. 3,053,179, patented Sept. 11, 1962, Raymond F. Reithel, "Photoconductolithography Employing Magnesium Salts."

Serial No. 45,943, now abandoned, Raymond F. Reithel, "Photoconductography Employing Spongy Hydroxide Images," continuation-in-part Serial No. 120,035, now U.S. Patent No. 3,106,518, patented Oct. 8, 1963, filed June 27, 1961.

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

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

Serial No. 45,946, now abandoned, Raymond F. Reithel, "Photoconductography Employing Molybdenum or Ferrous Oxide," continuation-in-part Serial No. 120,036, now U.S. Patent No. 3,106,156, patented Oct. 8, 1963, filed June 27, 1961.

Serial No. 45,947, now abandoned, Raymond F. Reithel, "Photoconductography Employing Cobaltous or Nickelous Hydroxide," continuation-in-part Serial No. 120,037, now U.S. Patent No. 3,057,788, patented Oct. 9, 1962, filed June 27, 1961.

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

Serial No. 45,949, now U.S. Patent No. 3,152,969, patented Oct. 13, 1964, Donald R. Eastman, "Photoconductolithography Employing Hydrophobic Images."

Serial No. 45,950, now U.S. Patent No. 3,106,516, patented Oct. 8, 1963, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Electrolytic Images to Harden or Soften Films."

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

Serial No. 45,952, now U.S. Patent No. 3,106,517, patented Oct. 8, 1963, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Spongy Images Containing Gelatin Hardeners."

Serial No. 45,953, now U.S. Patent No. 3,057,787, patented Oct. 9, 1962, John P. Sagura, "Photoconductography Employing Alkaline Dye Formation."

Serial No. 45,954, now U.S. Patent No. 3,178,362, patented April 13, 1965, John J. Sagura and James A. VanAllan, "Photoconductography Employing Quaternary

2

Salts."

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

Serial No. 45,956, now abandoned, 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, now U.S. Patent No. 3,095,808, patented July 2, 1963, Donald R. Eastman, "Photoconductolithography Employing Rubeanates."

Serial No. 45,959, now U.S. Patent No. 3,106,155, patented Oct. 8, 1963, Donald R. Eastman and Raymond F. Reithel, "Electrolytic Recording with Organic Polymers."

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

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

The object of the present invention is to provide a reliable inexpensive photoconductographic process, in which one or more prints are produced directly on paper or on paper which has received only inexpensive pretreatment.

It is a particular object of the invention to provide means for producing direct-positive prints on separate recording sheets. Because of this feature, any colors which are present in the photoconductive layer (for example to produce high sensitivity thereof) do not interfere with the final print which is formed for example on white paper support. Multiple copies of such positive prints are produced from a single exposure.

A further object of the invention is to produce these positive prints on separate recording sheets without the necessity of wetting the separate sheet thoroughly; prior photoconductographic processes involve thorough soaking of sheets (to make them electrically conducting) and this is most objectionable.

The present invention involves a transfer of a material, which may or may not be the image material, from the photoconductive layer and the separate species of the invention each have advantages of their own, all as discussed in further detail below. All embodiments of the invention have in common the electrolytic deposition (in accordance with the imagewise pattern produced by exposure of a photoconductive layer) of a chemical reducing agent or of an absorbing (sponge) material which receives (during deposit or subsequently) the chemical reducing agent.

Thus according to the invention the image pattern of variations in electroconductivity is produced in a photoconductive layer and either simultaneously with or immediately subsequent to the exposure, the layer is placed in contact with an electrolyte containing depositable ions of a chemical reducing agent or of a material which absorbs such an agent. An electric current is then passed through the layer, the current being distributed in accordance with the exposure pattern. This current causes the deposition of the chemical reducing agent directly or in an absorbing material, in a similar pattern on the photoconductive layer. Each of the various embodiments of the invention has this pattern of chemical reducing agent at one stage of the process.

In one embodiment of the invention a receiving sheet of paper is coated with a dye which is bleachable by reduction and the surface of the sheet is then pressed in contact with the reducing agent image which is on the photoconductive layer. The reducing agent bleaches the areas of the dyed paper which come in contact with the agent.

The paper with a positive image thereon is then separated from the photoconductive layer. In a preferred form of this embodiment the receiving sheet is first baryta coated, then coated with a hydrophilic colloid containing an acid adjusted to a pH between 2.0 and 6.0 to constitute a reduction inhibiting layer. That is, the reducible dye coated thereon tends to be stable in the presence of the acid. The stabilizing layer is then overcoated with an absorbent layer of hydrophilic colloid to which the dye is eventually applied before being pressed into contact with the photoconductively produced image of chemical reducing material.

Alternatively the paper, plain or with hydrophilic colloid coating thereon, may be pressed (without pre-dyeing) into contact with the electrolytically produced image of reducing material, to transfer some of the reducing material to the paper which is then dyed. The dye is applied substantially uniformly and certain areas thereof are bleached by reduction whereas the other areas of the paper (not covered by said agent) are dyed fully to constitute the positive print.

In either case, a succession of predyed, or subsequently dyed, papers may be pressed into contact with the electrolytically produced image of chemical reducing material, in order to produce a succession of prints. Prints far superior to prior direct positive photoconductographic prints are obtained by this process.

In another embodiment of the invention the separate receiving sheet is treated with a reducible diazo salt. When this receiving sheet is placed into contact with the image of chemical reducing material on the photoconductive layer, the diazo salt is reduced in the areas of the material. The receiving sheet is then separated from the photoconductive layer and is then treated with a solution of a diazo coupler to react with the unreduced diazo salt to form a dye in those areas which have not been in contact with the chemical reducing material. This diazo embodiment of the present invention is a particularly useful one. The diazo process is, of course, well understood and it may be applied directly with any of the well known materials. For example the diazo salt may be p-N-morpholino benzene diazonium-zinc chloride and the diazo coupler with which it is reacted may be 3-hydroxy-N-(β -hydroxyethyl)-2-naphthamide. Several prints which are direct positives and purple color may be made from a single photoconductographic image in this way.

In any of the embodiments of the present invention the photoconductive layer with its image of chemical reducing agent thereon may, before any of the subsequent steps, be treated with a second reducing agent which is absorbed by the first but not absorbed by other areas of the photoconductive layer. This strengthens the reducing effect of the plated image and this in turn produces a more contrasting final image and a larger number of copies when a succession of images are to be made. This is an example of the electrolytic deposition of a selective absorber which simultaneously or by later application absorbs the chemical reducing agent. In this particular case the absorber itself is also a chemical reducing agent.

In still another embodiment of the invention the receiving sheet is first coated with a hydrophilic colloid containing an oxidizing agent. The electrically produced image of reducing material when placed in contact with the oxidizing agent, reduces the latter in the areas corresponding to the exposed areas of the photoconductive layer. The residual positive image of oxidizing agent is then treated with an oxidizable colorless leuco dye to be oxidized to a color in the areas of unreduced oxidizing agent. A suitable oxidizing agent is colloidal manganese dioxide.

In still another embodiment of the invention the photoconductive layer with the image of chemical reducing material electrically deposited (directly or by absorption) thereon is treated with a solution of a reducible silver salt to form silver (along with unreduced silver salt) distributed on the layer in accordance with the image. A receiving sheet of paper is then pressed into contact with the

treated layer and some of the unreduced silver salt transfers to the paper. A reducing (developer) solution is then applied to the receiving sheet to reduce the transferred silver salt to silver to form a positive image thereon.

5 Excellent quality positive prints are obtained.

Indeed the quality of the prints obtainable by any of these embodiments (even if the image remains on the photoconductive layer and particularly when it is on a separate sheet) is far superior to that of photoconductographic prints made by prior methods. The $D_{\max}$ (maximum density) is higher and the background is clearer giving better contrast. The broader choice of reactions and the use of separate sheets of paper (plain or pre-treated) results in more stable images.

10 All prior systems in commercial use not only were limited to having prints on the photoconductive layer but in those cases involving separate coloring, they were limited to color destruction whereas some embodiments of the present invention employ color formation as discussed above.

Other objects and advantages of the various embodiments of the invention will be apparent from the following description when read in connection with the accompanying drawings in which:

25 FIG. 1 constitutes a flow chart schematically illustrating the formation of a photoconductographic image according to one embodiment of the invention;

FIG. 2 similarly illustrates an alternative arrangement in which the electrolytic deposition is simultaneous with the exposure;

FIG. 3 similarly illustrates one embodiment of the invention in which the photoconductographic image bleaches a pre-dyed receiving sheet;

FIG. 4 illustrates a preferred method for producing the receiving sheet shown in FIG. 3;

35 FIGS. 5, 6, 7 and 8 are flow charts schematically illustrating various embodiments of the invention;

FIG. 9 illustrates one application or enhancement of the reducing agent which constitutes the active image; this arrangement may be used in any of the embodiments of the invention.

40 In FIG. 1 an image of a positive transparency 10 illuminated by a lamp 11 is focused by a lens 12 on a photoconductive layer 15, for example of zinc oxide, carried on an electrically conducting support 16 which may be highly conducting paper or which preferably includes a metal foil layer. In this particular arrangement, the transparency 10 is moved to the left as indicated by the arrow 17 while the photoconductive layer 15 is moved to the right as indicated by the arrow 18 so that the image and the photoconductive layer move synchronously to expose the layer part at a time.

45 The exposed photoconductive layer 15 is then passed between electrodes 20 and 21 so that the photoconductive layer acts as a cathode in an electrolytic bath, the electrolyte being contained in the brush electrode 20. Thus an image 23 is formed on the photoconductive layer 15 in its areas which have been exposed and hence pass electric current. In the direct embodiment of the invention a chemical reducing material constitutes the deposit 23; in the indirect embodiments the deposit 23 is absorbent (sponge like) and may or may not be chemically reducing. In the indirect embodiments the reducing agent (or additional reducing agent) is applied to the absorbent material 23 either from the electrolyte in brush 20 or subsequently as shown in FIG. 9. In all embodiments an image of reducing agent 23 results from the photoconductographic step.

50 Photoconductographic processes in which the electrodepositing and the exposure take place simultaneously, may also employ the present invention. Such an arrangement is shown in FIG. 2 in which the transparency 10 is illuminated by a lamp 25 and diffusing sheet 26; in this case the lens 27 focuses an image of the whole transparency 10 onto the photoconductive layer 15. A trans-

parent electrode such as metal oxide coated on glass constitutes the anode 28. The electrolyte 29 containing depositable ions of chemical reducing material (and/or absorbent material) is placed between the layer 15 and the layer 28. When the switch shown schematically at 24 is closed, electric potential from the source 30 causes the depositable ions to coat in the exposed areas of the photoconductive layer 15.

The photoconductographically produced chemical reducing image is used in all embodiments of the invention.

In FIG. 3 a receiving layer 31 coated on a sheet of paper 32 is first dyed by a roller 33 and then pressed into contact with the photoconductographic image 23 by rollers 35 and 36. The material of the image 23 bleaches the dye in the layer 31 leaving clear or bleached areas 38 and dyed areas 39 which constitute a positive image of the original transparency 10 of either FIG. 1 or FIG. 2. For the sake of uniformity, the predyed paper sheet may be prepared as shown in FIG. 4 in which a layer of paper 40 is baryta coated as schematically shown at 41 and is then coated with a hydrophilic layer 42 applied by a roller 43, the hydrophilic layer may be gelatin held at a pH of 3.0. Another layer of colloid such as gelatin 45 is applied by roller 46 and this latter layer is dyed by the roller 33 to constitute the dyed layer 31, all corresponding to the receiving sheet shown in FIG. 3.

Specifically the colloid layer 42 in one example was a layer 0.003 inch thick (wet) of hardened gelatin consisting of 50 cc. of 5% gelatin plus 0.4 cc. wetting agent plus 1.2 cc. formalin adjusted to a pH of 3.0 with maleic acid all filtered through a balloon silk filter bag. This constitutes the reduction inhibiting layer 42. This was then overcoated 0.010 inch thick (wet) with 15% Superlose HA-11 adjusted to a pH of 5.5 with nitric acid. Superlose is a hydroxyethyl derivative of the amylose fraction of potato starch; it is supplied by Stein-Hall Company of New York in various forms, some of which include formaldehyde as a stabilizing agent. This constitutes the absorbent layer 45 ready for dyeing at roller 33 with a dye which is bleached by reduction.

A photoconductive image 23 for imagewise treatment of the dyed layer 31 is in this and the other examples discussed below, suitably prepared as shown in FIG. 1 or FIG. 2 by exposing a dye sensitized zinc oxide layer to a positive light image with an intensity of 400 foot candles, the time of exposure being 5 seconds. The conducting image is then developed electrolytically using a viscose sponge such as the brush 20 held at 80 volts positive with respect to the zinc oxide layer. The brush contains a solution of 1% manganese nitrate and development is complete after about 10 strokes with the brush. The image 23 itself in this case appears as a very pale yellowish image. It does not, of itself, have optical contrast suitable for use as the print.

The material from which the print image is eventually to be formed may include silver salts such as silver nitrate; a 5% solution of silver nitrate is suitable for this purpose. After a layer 31 containing silver nitrate is pressed into contact with the image 23 the metallic silver produced by the reducing action in this case, transfers to the image 23 and remains there. This leaves in the layer 31 only unreduced silver nitrate, distributed imagewise. The sheet is then swabbed or dipped in a developing solution of 2% hydroquinone plus 4% sodium sulfite plus 2% sodium carbonate. After 5 seconds it is dipped for 5 seconds in a photographic fixing solution and rinsed. A direct positive print which is light stable is thus produced. The silver nitrate in the Superlose overcoat is preferably adjusted so that no silver ion remains in the background area. If this is done very carefully the fixing may be eliminated, but in general it is simpler to have the fixing step. In this particular example the print density can be improved somewhat by including 10^{-5} mole per square foot of nickel sulfide in the Superlose overcoat to act as a nucleating agent. A slight modification of this process

is described in more detail in connection with FIG. 8 below.

Another example of the arrangement shown in FIG. 3 is as follows: The reducing image 23 is deposited directly from an electrolyte developer containing 1% magnesium sulfate plus 1% sodium sulfite. The recording layer 31 is dyed by the roller 33 so as to contain 0.4% of a triphenyl-methane dye (Malachite Green EK-1264) in 10% gelatin plus 2% formalin plus 1% wetting agent coated 0.005 inch thick (wet) on baryta coated paper. Upon contact with the image 23 the sulfite reduces the Malachite Green to a colorless form in the areas of the reducing image. This results in a green direct positive image on the separate recording sheet 32.

In FIG. 5 the image 23 is pressed between rollers 35 and 36 into contact with a paper 50 carrying a colloid layer 51 which is perfectly clear. Some of the reducing agent 23 transfers to the layer 51 so that when it is dyed by a roller 52 certain areas 53 remain bleached and the other areas 54 become dyed to constitute a positive print. Thus FIGS. 3 and 5 constitute alternatives in which the dye is applied respectively before and after the transfer step.

In FIG. 6 the image of reducing agent 23 is pressed between rollers 35 and 36 into contact with a layer 60 containing a diazo salt which is reduceable by the agent 23. The reduced diazo salt remains clear in areas 61 but reduces to form a dye in area 62 when brought into contact with a diazo coupler applied by means of roller 63. As an example of this diazo reaction, the reducing image 23 is prepared as shown in FIGS. 1 (or 2) and 9 by depositing an absorbent material with a reducing agent absorbed therein, from an electrolyte containing 0.8% magnesium nitrate which is then swabbed with a solution of 2% hydroquinone plus 2% sodium sulfite which is absorbed by the electro deposited image which is itself slightly reducing as well as absorbing. This additional treatment increases the reducing properties of the electrolytically deposited image. The layer 60 is coated 0.003 inch thick (wet) from a solution containing 5% gelatin plus a diazo salt (p-N-morpholine benzene diazonium-zinc chloride). After it has been rolled into contact with the reducing image 23, the unreduced diazo salt (corresponding to the non-image areas of the reducing image 23) is then treated (by roller 63) with a coupler solution consisting of 0.5% of 3-hydroxy-N-(β -hydroxyethyl)-2-naphthamide dissolved in an alkaline 50:50 water-alcohol mixture. The image 23 (once prepared) may be pressed successively into contact with several receiving sheets containing the diazo salt; thus several prints are produced, all of good contrast.

In FIG. 7 the reducing image 23 is pressed between rollers 35 and 36 into contact with a layer 70 containing an oxidizing agent. For example the image 23 may be produced from an electrolyte or developer containing 1% magnesium sulfate plus 1% ferrous sulfate. The layer 70 contains colloidal manganese dioxide formed by adding 0.2% solution of potassium permanganate to 50 cc. of 5% gelatin and coating 0.003 inch thick (wet) onto a baryta coated paper.

The unreduced manganese dioxide in the layer 70 is adequate to oxidize a leuco dye applied by a roller 71. Oxidizable leuco dyes are well known, one of the commonest being National Solvat Blue 0, supplied by National Aniline Company. Again a direct positive image results consisting of dyed areas 72 and clear areas 73, the latter not having been oxidized. Three or four prints of good contrast may be made from a single reducing image 23 by this method.

In FIG. 8 the reducing image 23 on the zinc oxide layer 15 is first overcoated with a silver nitrate solution 80 either by direct coating as shown or by first coating with a 5% gelatin layer 0.003 inch thick when wet and then swabbing the gelatin layer with silver nitrate solution. Either way silver nitrate in gelatin is coated on the re-

ducing image 23. A separate recording sheet 81 is coated 0.005 inch thick (wet) with a colloid layer 82 consisting of a 15% solution of Superlose HA-11 adjusted to a pH of 5.5 with nitric acid. This sheet 81 is rolled into contact with the treated image 23 forming reduced silver adjacent to the image 23 and unreduced silver nitrate in the other areas of layer 80. The unreduced silver nitrate is absorbed by the colloid layer 82 which is then passed in contact with a roller 83 so that photographic developer is applied (2% hydroquinone plus 4% sodium sulfite plus 2% sodium carbonate). A direct positive print of clear areas 85 and silver areas 86 is thus produced on the support 81.

The Malachite Green example discussed in connection with FIG. 3 may also be employed in the arrangement shown in FIG. 8. In this case the Malachite Green is swabbed onto the reducing image 23 (instead of applying silver nitrate solution thereto). Part of the Malachite Green is then reduced by the image 23 and the unreduced Malachite Green remaining in the layer 80 (of FIG. 8) is absorbed in the separate recording layer 82, consisting, in this example, of a coating of 5% gelatin coated 0.005 inch thick (wet) on baryta paper. Again a direct positive clear image results on the separate recording sheet 81 and again several copies can be made from one master.

In FIG. 9 is illustrated the general step of applying additional reducing agent 90 which is absorbed by the image 23 (which may or may not be reducing) but not absorbed by the clear areas 91 of the zinc oxide layer 15. The main advantage of this additional step which is useful in several embodiments of the invention, is the fact that the deposited image 23 need not be as dense and hence less exposure or less development time is required in the production of the image 23.

Having thus described several of the very successful examples of our invention, we wish to point out that it is not limited to the specific arrangements shown but is of the scope of the appended claims.

I claim:

1. In a photoconductography process in which an image pattern of variations in electrical conductivity are produced in a photoconductive electrode layer, the steps comprising electrolytically cathodically depositing on the electrode layer, a spongy metallic hydroxide image distributed in accordance with said pattern, applying to the spongy image a chemical reducing agent, placing said image with its reducing agent into firm contact with the surface of a separate receiving sheet to transfer reducing agent to said surface and chemically reducing, on said surface in accordance with the pattern of transferred agent, a material which, upon reduction, changes its color characteristics.

2. A process according to claim 1 in which the surface of the receiving sheet is a colorless colloid and including the steps of separating the colorless colloid with the pattern of transferred agent from the electrode and then applying a reducible dye to said surface.

3. A process according to claim 1 in which the surface of said separate sheet is predyed with a dye which is bleached by reduction and in which said dye is so bleached during said pressing step.

4. The process according to claim 1 in which said separate sheet contains a diazo material which upon chemical reduction becomes color-forming and including the step of separating the separate sheet with the imagewise reduced diazo material therein, and then applying to said surface, a diazo color coupler which with the reduced diazo material forms a dye.

5. A process according to claim 4 in which the diazo salt is p-N-morpholine benzene diazonium-zinc chloride and is coated in gelatin on baryta coated paper and in which the diazo coupler is 3-hydroxy- β -hydroxy-ethyl-2-naphthamide dissolved in an alkaline 50:50 water alcohol mixture.

6. A process according to claim 1 which said separate sheet contains an oxidizing agent which is reduced during said pressing step and including the steps of separating the sheet from the electrode layer and treating said surface with a leuco material which is oxidized to a dye in the unreduced areas.

7. A process according to claim 1 including the steps of applying a silver salt solution substantially uniformly to said electrode layer with the spongy image containing reducing agent before said pressing step, whereby the silver salt is imagewise reduced to silver and remains on said spongy image and the unreduced silver halide in the non-image areas is transferred during said pressing step to the surface of said receiving sheet, separating said receiving sheet from the electrode layer and applying to said surface a second reducing agent to reduce the transferred silver halide to silver.

8. A process according to claim 1 in which the electrolyte in contact with the electrode layer during said image depositing step contains a reducing agent which is deposited in and simultaneously with said spongy image.

9. A process according to claim 1 in which the reducing agent is applied to the spongy image subsequent to the depositing step and before the pressing step.

10. A process according to claim 1 in which the receiving sheet is first baryta coated, then coated with a hydrophilic colloid containing an acid adjusted to a pH between 2.0 and 6.0 to constitute a reduced inhibiting layer, and then coated with an absorbent layer of a hydrophilic colloid.

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DAVID KLEIN, *Primary Examiner*.