Feb. 22, 1966 R. W. BAXENDALE ETAL 3,236,749

SINGLE-STEP DIRECT IMAGE-FORMING ELECTROLYTIC DEVELOPER AND PROCESS FOR PHOTOCONDUCTOGRAPHIC PROCESSING

Filed Feb. 13, 1962

Fig. 1

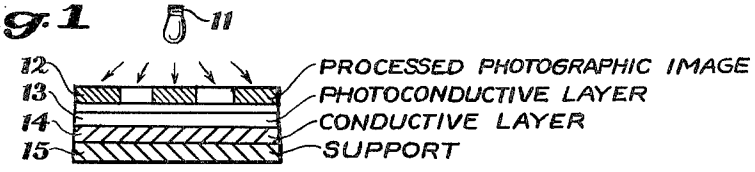


Fig. 2

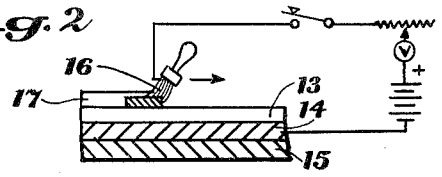


Fig. 3

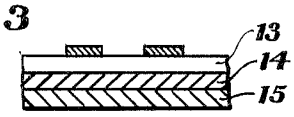
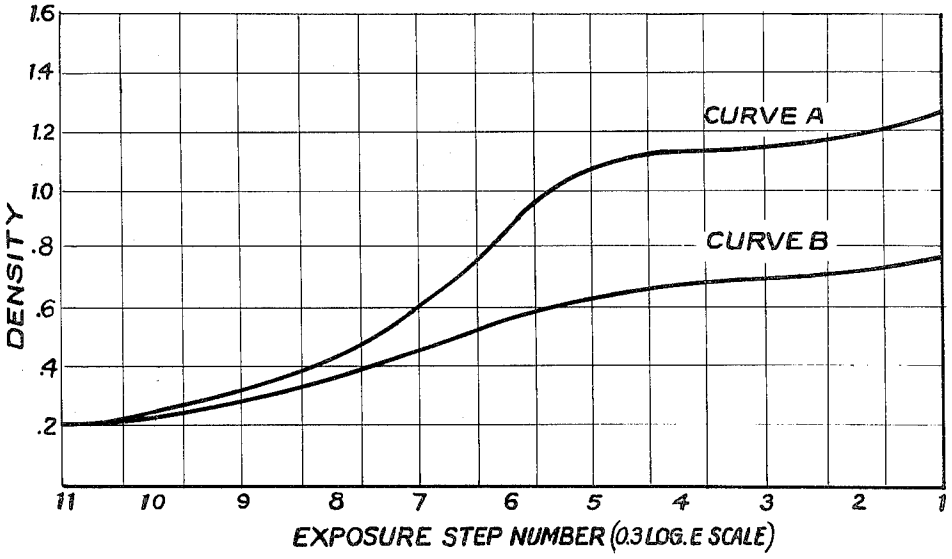


Fig. 4



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United States Patent Office 3,236,749 Patented Feb. 22, 1966

3,236,749

SINGLE-STEP DIRECT IMAGE-FORMING ELECTROLYTIC DEVELOPER AND PROCESS FOR PHOTOCONDUCTOGRAPHIC PROCESSING

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Filed Feb. 13, 1962, Ser. No. 173,056
13 Claims. (Cl. 204—18)

This invention relates to photoconductography and more particularly to a novel developer solution for single-step direct image-forming photoconductographic processing.

Photoconductography is the process of producing images by using photoelectrically sensitive materials to control the electrolytic deposition or formation of a material capable of being the image or capable of being converted to the image by other means. It forms a complete image at one time or at least a non-uniform part of this image as is distinguished from facsimile which at any one time produces only a uniform dot.

Photoconductography is described in detail in British Patent 188,030, von Bronk, and British Patent 464,112, Goldman, modifications being described in British 789,309, Berchtold and Belgian 561,403, Johnson et al.

The present invention is concerned with those processes of photoconductography in which the production of the image is brought about by a single-step direct image-forming electrolytic developer. Single-solution or single-step electrolytic developers used in this process are to be distinguished from those developers in which the electrolytic deposition or formation of a faintly visible image material is subsequently made visible by a second step, which may be chemical, electrical, or mechanical. Single-solution electrolytic developers are those developers which will produce a useful visible image material by a single electrolytic development step and require no further treatment for image formation. The present invention pertains to processes of photoconductography in which the image is formed simultaneously with exposure of the photoconductive layer or in which the image is developed after exposure has terminated. (See Franz Urbach U.S. application Serial No. 64,901, filed October 25, 1960).

The present invention also pertains to processes of photoconductography without regard for the particular method used for bringing about development of the image. For example, widely diverse techniques can be employed in development to apply and distribute the developer solution over the photoconductive layer of the photoconductographic material, such as the use of an angular sweeping blade for distributing the electrolytic developer as provided by an automobile windshield wiper, a viscose sponge containing developer solution, a transfer roller covered with developer solution, a rotary brush containing developer solution, etc. Another suitable technique involves distributing the electrolytic developer over the surface of the print-forming layer in the area between a surface transparent electrode and the photoconductive layer.

The present invention provides an electrolytic developer which can be employed for image development in processes of photoconductography where a wide variety of photoconductive layers are employed. For example, the photoconductive layers can comprise zinc oxide or other suitable light colored photoconductors in a suitable insulating resinous binder. The photoconductive layers can also contain sensitizing dyes or other sensitizing materials in which a higher level and range of sensitivity is obtained in a given spectral region or spectral sensitization can be brought about in more than one spectral region.

Included among the photoconductographic elements that are developed advantageously with our single-step direct image-forming developers are the elements described in Johnson et al. U.S. Patent 3,010,884, issued November 28, 1961.

Single-solution electrolytic developers are known in the art of electrolytic recording. For example, Australian Patent 215,754, complete specification published October 3, 1957, describes the use of a nickelous salt with sodium thiosulfate pentahydrate as an electrolytic developer for processing photoconductive zinc oxide paper by photoconductography.

Many of the prior art single-step direct image-forming electrolytic developers have not produced images having as high a contrast and density as is desired.

It is, therefore, an object of our invention to provide a novel class of single-solution, one-step electrolytic developers for photoconductographic processing.

Another object of our invention is to provide for photoconductography, an electrolytic developer that can produce images having higher densities and gamma (contrast) than those produced from single-solution developers where noble-metal ions are used as the image-forming material.

Another object of our invention is to provide for photoconductography, an electrolytic developer which produces an image material stable to light, fingerprinting, mild chemical treatment such as that used in bleaching the dyes necessary for sensitizing the zinc oxide layers, and to smearing.

These and other objects that are apparent from the following specification and claims are accomplished according to our invention by the use of our novel single-step direct image-forming electrolytic developers.

Our electrolytic developer in its simplest form comprises a water solution of a water-soluble, ionizable iron compound, and a water-soluble material which is electrolytically decomposable to form sulfide ions.

We have found that it is advantageous to include in the developer a water-soluble ionizable nickel compound and an anti-shorting agent such as magnesium acetate or calcium acetate.

The iron compound used in our developer solution is any water-soluble ionizable iron compound including compounds such as ferrous acetate, ferrous bromide, ferric bromide, ferrous chloride, ferric chloride, ferrous nitrate, ferric nitrate, ferric oxalate, ferrous sulfate, ferric sulfate, ferrous thiocyanate, ferric thiocyanate, ferrous thiosulfate, etc. It is advantageous to use these compounds in their hydrated form where hydrates are available because of their higher solubilities.

The water-soluble material which is electrolytically decomposable to form sulfide ions includes any sulfur-containing compound which generates sulfide ions during cathodic reduction such as the water-soluble thiosulfates, e.g., sodium thiosulfate, potassium thiosulfate, ammonium thiosulfate, calcium thiosulfate, magnesium thiosulfate, etc., and organic sulfides such as thiobarbituric acid, mercaptosuccinic acid, thiourea, etc., the thiouronium compounds, e.g., 3-S-thiouroniumpropane sulfonate, etc., the isothiouronium compounds, e.g., ethyl isothiouronim chloride, 2,5-dihydroxyphenylisothiouronium chloride, etc., the thiosemicarbazide compounds, e.g., thiosemicarbazide, potassium sulfomethylthiosemicarbazide, etc., 2-mercaptothiazoline, 2-thiophene carboxylic acid, etc., and polymeric sulfides, e.g., the 2-hydroxyethylaminooligoethylene sulfide in which n has an average value of 1.7 (e.g., the average number of ethylene sulfide groups per molecule in the oligomeric

mixture is 1.7), the morpholinooligoethylene sulfides in which n has an average value of 1.4, etc.

The water-soluble ionizable nickel salts that are used to advantage in our developers include nickel acetate, nickel bromide, nickel chloride, nickel nitrate, nickel sulfate, etc.

When it is desired to use a single compound to supply both the iron ions and the material electrolytically decomposable to produce sulfide ions, a compound such as ferric thiosulfate, ferrous thiosulfate, etc., may be used to advantage.

The concentration of the components in our electrolytic developer solution is varied over wide ranges. The preferred concentration of the iron compound is in the range from 0.7 to 10% and the preferred concentration of a compound such as sodium thiosulfate is in the range from 1.5 to 5.0%. When nickel sulfate is used the preferred concentration is in the range from 0.1 to 0.5%.

The developer solution is applied to the photoconductographic material in any convenient way so that there is a film of the developer solution covering the photoconductor surface to be developed. For example, the developer may be applied with a roller applicator, a sponge, a brush, poured over the photoconductor surface and then distributed by some suitable means, or the photoconductographic element may be immersed in a tray containing the developer solution so that it covers the photoconductive surface. The developer solution may be applied to the photoconductor surface either before or after exposure of the element to the light image. When the developer is applied before exposure, it is possible to perform the electrolysis either during or after exposure. For the electrolytic development, the conducting layer of the photoconductographic element is made the cathode and an anode is then placed in contact with the developer solution so that in those areas where the photoconductor has been exposed to light and is thus made electrically conducting, there is a cathodic deposition of iron sulfide from the developer solution. The anode used in this process may take on a wide range of form, for example, it may be a stationary rod, plate, or transparent surface film, or it may be a moving electrode which may or may not be used simultaneously to apply the developer solution, such as a roller, brush, viscose sponge, etc. When a moving electrode is used, electrolysis takes place as the electrode is moved across the photoconductor layer. Since the moving type of electrode electrolyzes only a part of the photoconductor surface at a given time, higher current densities are applied for a given total current than would be possible with a fixed electrode. A wide range of voltages may be used for effecting the electrolytic development, for example, the voltage may range from the lowest voltage which is capable of forming an iron sulfide image up to the breakdown potential of the photoconductive layer and yield good results. Voltages of from 40 to 70, however, are preferred for typical photoconductographic materials.

Since the photoconductive layers act as rectifiers, alternating current as well as direct current can be used in the practice of our invention. Our invention is not limited to any particular mode of development. Practically all photoconductographic developing systems can be used to advantage with our developers.

The single-step direct image-forming electrolytic developers of our invention and their use are further illustrated by the following specific examples, which are illustrative and are not to be considered as limiting the scope of our invention.

Example 1

A dye-sensitized zinc oxide layer on a conducting support was exposed to 400-foot candle tungsten illumination through a 0.3 density increment step-wedge for 5 seconds. The resulting image was then developed electrolytically using a viscose sponge brush electrode held at 70 volts potential positive with respect to the zinc oxide layer, and a water solution containing 0.7% ferrous sulfate heptahydrate plus 1.5% sodium thiosulfate pentahydrate. A black image was produced in the form of and relative to the amount of the initial exposure, on the surface of the zinc oxide layer. The reflection density of the image produced by this electrolytic developer in the region of highest exposure (2000-foot candle seconds) was 1.2 density units.

Images produced from a solution of silver nitrate-thiourea on a similar zinc oxide layer exposed to 2000-foot candle seconds had a reflection density of only 0.72 density unit.

The neutral black images produced by use of our developer solutions can be tinted if this is desired by including a sufficient amount of a water-soluble ionizable metal salt which produces a colored metal sulfide. For example, antimony sulfide will tint the image reddish-orange, arsenic sulfide and cadmium sulfide will tint the image yellow, cobaltous sulfide will tint the image brown, manganous sulfide will tint the image green, magnesium sulfide will tint the image red, etc.

The following examples will illustrate other typical developers of our invention and will show the unexpected density and gamma values obtained with them as compared to the densities and gammas obtained with a nickel chloride sodium thiosulfate developer.

Example 2

A sheet of dye sensitized zinc oxide in a resinous binder (80% Pliolite S–7, a synthetic styrene copolymer resin made by Goodyear Tire and Rubber Co. and 20% organosilicon oxide polymer) coated on an aluminum foil-paper laminate was exposed for 10 seconds to 400-foot candle tungsten illumination through a 0.3 density increment photographic step-wedge. After exposure, the conducting image areas of the photoconductor were developed electrolytically using a water solution containing 0.75% $FeSO_4 \cdot 7H_2O$+1.5% $Na_2S_2O_3 \cdot 5H_2O$+0.1% $NiSO_4 \cdot 6H_2O$, contained in a viscous sponge brush electrode, held at 70 volts potential, positive with respect to the zinc oxide layer and using 10 strokes of the sponge at the rate of 1 stroke per second. The resulting iron sulfide image material had a density of 1.20 and a gamma of 0.80.

A similar sheet of zinc oxide material was exposed as described and developed with a water solution containing 0.75% $NiCl_2 \cdot 6H_2O$+1.5% $Na_2S_2O_3 \cdot 5H_2O$, to produce an image material having a density of only 0.75 and a gamma of only 0.33.

Example 3

A sheet of the dye-sensitized zinc oxide photoconductographic material described in Example 2 was exposed and developed as in Example 2 but using a developer solution containing 10 percent $FeSO_4 \cdot 7H_2O$ + 5% $Na_2S_2O_3 \cdot 5H_2O$+0.5% $NiSO_4 \cdot 6H_2O$ and 40 volts potential. The image maximum density was 1.12 and the gamma was 0.80.

Another sheet of the same photoconductographic material was exposed as in Example 2 and developed as described using an aqueous developer solution containing 10 percent $NiCl_2 \cdot 6H_2O$+5% $Na_2S_2O_3 \cdot 5H_2O$. The maximum density produced was only 0.92 and the gamma was only 0.45.

Example 4

A sheet of the dye-sensitized zinc oxide photoconductographic material described in Example 2 was exposed and developed as in Example 2 with an aqueous developer solution containing ferrous sulfate and thiourea to produce a good black image.

Similar results were produced with a developer containing thiobarbituric acid in place of thiourea.

Our developer solutions have good stability upon keeping, excepting for the developers in which the thiosulfate ion is used as the material to furnish sulfide ions during the development step. We have found that the thio-

sulfate ion containing developers can be stabilized advantageously by the addition of a water soluble alkaline earth sulfite or bisufite, such as calcium sulfite, calcium bisulfite, magnesium sulfite, magnesium bisulfite, etc., to the developer solution. Although these stabilizing compounds are used advantageously over a wide range of concentrations, the preferred range is from 1.5 to 5.0 percent by weight based on the amount of the thiosulfate pentahydrate salt used in the developer. If it is not desired to use the stabilizer in the thiosulfate ion containing developer, it is perferable to mix the developer not more than a day or two before use or else mix the water-soluble compound supplying iron ions in an "A" solution and the thiosulfate compound in a "B" solution which can be stored for long periods of time and then mixed as needed before use.

Our invention is still further illustrated by the accompanying drawings, FIG. 1, FIG. 2, FIG. 3, and FIG. 4.

In FIG. 1, light from light source **11** is passed through the processed photographic image **12** to expose the light-sensitive photoconductive layer **13** that is coated on the conductive layer **14** which is on support **15**.

In FIG. 2, the light exposed image in the left-hand portion of layer **13** has been developed electrolytically by the passage of a direct current through the film **17** of aqueous ferrous sulfate, sodium thiosulfate developer solution of Example 1 applied by the viscous sponge **16** which serves as an anode and the light exposed conducting areas of the photoconductive layer areas which are made the cathode.

FIG. 3 shows the completely developed iron sulfide image on layer **13** made by the process illustrated by FIG. 2.

FIG. 4 shows sensitometric curves A and B relating the density and the logarithm of the exposure producing the density. Curve A was obtained from the print produced in Example 2 using our developer solution containing water, ferrous sulfate, sodium thiosulfate and nickel sulfate. Curve B was obtained from the print produced in Example 2 using a developer containing water, nickel sulfate and sodium thiosulfate.

The novel single-step direct image-forming electrolytic developer solutions of our invention are valuable for developing image exposed photoconductographic elements. Our aqueous developer solutions contain a water-soluble ionizable iron compound and a water-soluble material which decomposes upon electrolysis to produce sulfide ions. We have found that it is advantageous to include a water-soluble ionizable nickel compound and an anti-shorting agent such as magnesium acetate or calcium acetate. Our developers are distinguished from other electrolytic developers by producing images with unexpectedly high maximum densities and gammas. For example, the maximum density produced by our developers is as much as 60% higher than the densities produced by a corresponding nickel-thiosulfate developer. Similarly, our images have gammas that are up to 140% higher than those produced with a corresponding nickel thiosulfate developer. The ingredients used in our developers are inexpensive and readily available.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of:

(1) iron ions; and

(2) a water-soluble material selected from the class consisting of the water-soluble thiosulfates, the water-soluble organic sulfides, the water-soluble thiouronium compounds, the water soluble isothiouronium compounds, the water-soluble thiosemicarbazide compounds, and the water-soluble polymeric sulfides;

(3) a water-soluble ionizable nickel salt.

2. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of:

(1) iron ions;

(2) a water-soluble material selected from the class consisting of the water-soluble thiosulfates, the water-soluble organic sulfides, the water-soluble thiouronium compounds, the water-soluble isothiouronium compounds, the water-soluble thiosemicarbazide compounds and the water-soluble polymeric sulfides;

(3) a water-soluble ionizable nickle salt; and

(4) a compound selected from the class consisting of calcium acetate and magnesium acetate.

3. A single-step process for electrolytically developing photoconductographic material comprising a conducting layer coated with an image exposed photoconducting layer, said electrolytic development comprising the steps of:

(1) applying a single-step direct image-forming electrolytic developer containing an aqueous solution of iron ions and a water-soluble material selected from the class consisting of water-soluble thiosulfates, the water-soluble organic sulfides, the water-soluble thiouronium compounds, the water-soluble isothiouronium compounds, the water-soluble thiosemicarbazide compounds and the water-soluble polymeric sulfides; and

(2) passing an electrolyzing current through the said developer between an anode in contact with it and the image exposed areas of said photoconducting layer as the cathode, such that a corresponding iron sulfide image is deposited on the surface of said photoconducting layer.

4. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of an ionizable iron salt, nickel sulfate, and an ionizable thiosulfate salt.

5. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of ferrous sulfate, nickel sulfate, and an alkali metal thiosulfate.

6. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of ferrous chloride, an ionizable nickel salt, an alkali metal thiosulfate.

7. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of ferrous nitrate, an ionizable nickel salt, and an alkali metal thiosulfate.

8. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of ferrous acetate, an ionizable nickel salt, and an alkali metal thiosulfate.

9. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of an ionizable iron salt, and ionizable nickel salt, and an ionizable thiosulfate salt.

10. A process of claim **3** in which the single-step direct image-forming electrolytic developer for photoconductographic processing contains an aqueous solution of an ionizable iron salt, an ionizable nickel salt, and and ionizable thiosulfate salt.

11. A process of claim **3** in which the single-step direct image-forming electrolytic developer for photoconductographic processing contains an aqueous solution of an ionizable iron salt, an ionizable nickel salt, an ionizable thiosulfate salt, and a compound selected from the class consisting of calcium acetate and magnesium acetate.

12. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of iron thiosulfate, and a compound selected from the class consisting of a water-soluble alka-

line earth sulfite and a water-soluble alkaline earth bisulfite.

13. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of iron thiosulfate and a compound selected from the class consisting of calcium sulfite, calcium bisulfie, magnesium sulfite, and magnesium bisulfite.

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