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PHOTOCONDUCTOGRAPHY EMPLOYING ALKALINE DYE FORMATION

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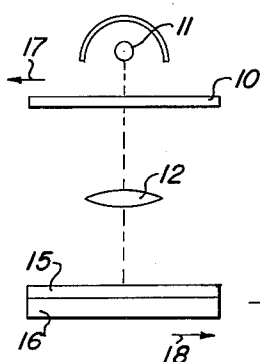


Fig. 1

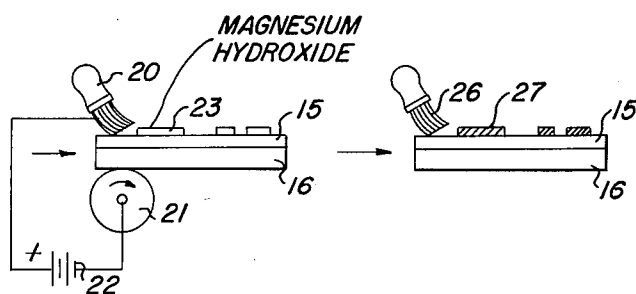
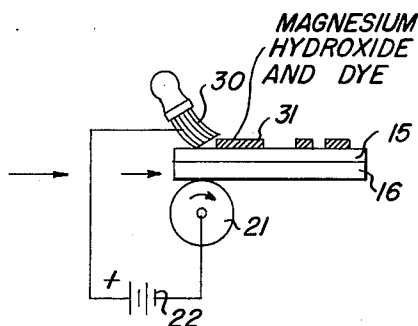


Fig. 2



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PHOTOCONDUCTOGRAPHY EMPLOYING ALKALINE DYE FORMATION

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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 co-filed applications:

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

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

Serial No. 45,942, Raymond F. Reithel, "Photoconductolithography Employing Magnesium Salts."

Serial No. 45,943, Raymond F. Reithel, "Photoconductography Employing Spongy Hydroxide Images," now abandoned, continuation-in-part Serial No. 120,035, filed June 27, 1961.

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, 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, continuation-in-part Serial No. 120,037, filed June 27, 1961.

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, 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. 45,954, John J. Sagura and James A. Van Allan, "Photoconductography Employing Quaternary Salts."

Serial No. 45,955, Franz 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."

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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, Van Bronk, and British 464,112, Goldmann, modifications being described in British 789,309, Berchtold, and Belgium 561,403, Johnson et al. The present invention relates particularly to those photoconductographic processes in which the final print is formed directly on the photoconductive layer used in the process.

The object of the present invention is to provide a process giving higher contrast, higher D max. and higher speed than prior systems of photoconductography.

One feature of the present invention is that the electrolytic or photoconductographic deposit itself is not visible or just barely visible and is not suitable as a final image. This feature may be used wherever it is desirable to deposit an invisible or substantially invisible image.

However, the main advantage of this system is the fact that it permits the use of electrolytes which deposit an adequate image (although invisible) quite rapidly and quite firmly on the photoconductor. The coloring step may be simultaneous with or subsequent to the deposition of the image.

According to the preferred embodiment of the invention the electrolyte is an aqueous one containing magnesium ions. Zinc oxide in resin is normally used as the photoconductor which is exposed usually a line at a time to the light image to be recorded. Magnesium hydroxide is then deposited electrolytically on the more conducting areas of the exposed zinc oxide layer. The magnesium hydroxide image is substantially invisible. However the areas of the zinc oxide which are covered with magnesium hydroxide are highly alkaline and the other areas are substantially neutral.

According to the second step of the invention, at least in the embodiment just described, the magnesium hydroxide image is rendered quite dense (optically) by treatment with a material such as a diazonium salt or a pyridinium compound, which forms a visible dye at the alkaline pH of magnesium hydroxide but does not form a dye in the uncoated areas of the zinc oxide photoconductor. Examples of suitable dye reagents and reactions are described below.

In one preferred embodiment of the invention, the color forming material is incorporated in the electrolyte itself, the color former being one which is colorless even in a slightly alkaline solution but which becomes highly colored at the highly alkaline pH of the deposited magnesium hydroxide.

In general the electrolyte action tends to form a higher pH condition right at the cathode (especially when the aqueous electrolyte used is approximately neutral) and when the color former is included in the electrolyte itself this is adequate to deposit the dye itself as an image.

A preferred embodiment of the invention employs an approximately neutral pH wetting agent (such as the ordinary household detergents) in the electrolyte and in the solution of color former to speed up contact with the magnesium hydroxide image. In the single solution embodiment (i.e. the electrolyte containing both the magnesium ions and the dye former) such neutral wetting agent is included in the electrolyte giving improved speed and contrast.

The invention and its advantages will be fully understood from the following description of the accompanying drawings and of specific examples.

In the drawings:

FIG. 1 is a schematic flow chart illustrating one embodiment of the invention.

FIG. 2 similarly illustrates an alternative embodiment in which two of the steps of the process shown in FIG. 1 are combined into a single step.

In FIG. 1 a negative transparency 10 is illuminated by a lamp 11 and an image thereof is focused by lens 12 on a zinc oxide photoconductive layer 15 carried on a conducting support 16. The transparency 10 is moved to the left as indicated by the arrow 17 and the photoconductive layer 15, as indicated by the arrow 18, is moved to the right synchronously with the image of the transparency 10. Other photoconductors may be used, particularly if the electrolytic development takes place during exposure rather than immediately subsequent thereto as illustrated in FIG. 1. The exposed photoconductive layer 15 carrying the imagewise distribution of increased conductivity is passed between a brush 20 carrying electrolyte and a roller 21 to permit electrolytic action created by a source of potential indicated at 22. The layer 15 acts as the cathode in this case. The brush 20 contains an electrolyte having magnesium ions therein. These ions combine with the excess hydroxide ions at the cathode, forming magnesium hydroxide on the conducting areas of the layer 15. The magnesium hydroxide is barely, if at all, visible on the zinc oxide layer. However, the surface including the magnesium hydroxide image and the uncoated areas of the layer 15, is then treated with a second solution by a brush 26. This solution contains a reagent which becomes a dye at the high alkaline pH of the magnesium hydroxide thus forming a permanent image 27 of high optical density, directly on the photoconductor 15. Examples of dye formers are discussed below.

FIG. 2 combines the electrolytic step and the dye forming step so that the solution applied by the brush 30 contains both magnesium ions and a material which is colorless at the pH of the solution but which becomes high density dye at the higher pH associated with magnesium hydroxide which is deposited by electrolytic action on the zinc oxide layer 15. The resulting image 31 contains magnesium hydroxide and the high density dye which constitutes the final image or print.

In either FIG. 1 or 2, the D.C. source 22 may be replaced by an A.C. source since the zinc oxide in contact with the electrolyte acts as a rectifier.

Example 1

A sensitive zinc oxide in resin layer on aluminum foil was exposed to a negative pattern for 1 second at 400 foot candles. The conductivity image was then electrolytically developed to an invisible image of magnesium hydroxide by swabbing the surface of the photoconductor with a cellulose sponge (positive) electrode containing an aqueous magnesium chloride solution while applying an 80 volt potential between the sponge and the metal backing of the zinc oxide layer. For smooth uniform application of the electrolyte to the photoconductor, the electrolyte preferably contains a detergent cream such as commonly supplied by cosmetic manufacturers; for example those containing petrolatum, lanolin derivatives and sodium octylphenoxyethoxyethyl ether sulfonate are readily available and are satisfactory. The invisible magnesium hydroxide image is then developed to a visible image by treatment with a second reagent, with no electric potential being applied. In this example, one-half percent solution of 1-methyl-2-(2,4-dinitrobenzyl) pyridinium p-toluenesulfonate containing one percent of the detergent cream just mentioned, produced a violet positive image. Alternatively the second developer may contain a product which reacts with the magnesium hydroxide and another reagent which then reacts with the first one to form the colored image.

Example 2

The magnesium hydroxide image was prepared as in Example 1 which was then treated with a 1% detergent

solution containing a diazonium salt and phloroglucinol, to produce an azo dye image.

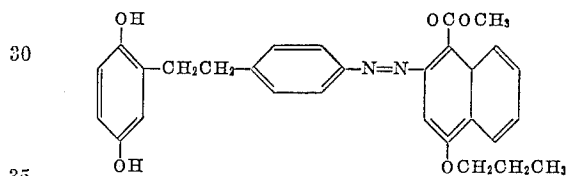
Example 3

Prints were made as in Examples 1 and 2 but without the detergent cream. High density images were produced but the sharpness of the image was slightly poorer than in Examples 1 and 2.

Example 4

A piece of high wet-strength paper was moistened with an aqueous solution containing one-half percent magnesium chloride. This moistened paper was put into contact with a previously exposed sheet of photoconductive recording material consisting of zinc oxide in the usual resin binder, coated on aluminum foil and a metal roller was connected to the positive side of an 80-volt power supply. The aluminum foil backing was connected to the negative side of the supply. The paper was removed from contact with the recording material and was swabbed with an aqueous solution containing one-half percent of 1-methyl-2-(2,4-dinitrobenzyl) pyridinium paratoluene sulfonate. A dark violet negative image of high contrast and high density was formed on the paper.

It is noted that 1-acetoxy-2-[p-(β -hydroxyethoxy)-phenylazo]-4-propoxynaphthalene is sensitive either to increased temperature or to increased alkalinity. The formula is as follows:



A solution of 20 g. of the above in 26 cc. of n-butylacetanilide and 40 cc. of cyclohexanone was prepared by stirring the ingredients at 70° C. This solution was added in a thin stream of 200 g. of 10% gelatin and 5 percent of Alkanol B solution which was stirred vigorously at 50° C. The dispersion was (five times) passed through a colloid mill set at 0.01 inch. The mill was washed with 10 cc. of warm distilled water and the washings were combined with the dispersion. The dispersion was solidified by the chill-plate method and cut to noodles 2-3 mm. in diameter; the noodles were washed 6 hours in hard water at 5° C. with agitation and a water flow of 670 cc./minute. At this stage the dye-containing solvent particles were less than 1 μ in diameter. The weight of dispersion was 395 g.; samples of the dispersion were still stable at the end of three weeks of storage at 50° C.

The bright yellow dispersion (three parts) was diluted with distilled water (four parts) and coated by the chill-plate coating-knife technique on a baryta paper support at 7 cc./ft.².

The paper thus coated was moistened with a dilute aqueous electrolyte and placed in contact with a layer of zinc oxide containing an imagewise distributed variation in conductivity. A conductor was placed on top of the paper and 80 ma. current from a 60 volt source was passed for 5 seconds through the paper and through the conducting areas of the zinc oxide layer. The image-wise alkalinity formed by the image-wise discharge of hydrogen ions at the cathode gave a negative magenta image proportional to the current flow. The non-image yellow dye background remained unchanged.

Any metal whose hydroxide is substantially insoluble is useful to provide the alkalinity for the dye formation, but magnesium is the most preferred for several reasons, mainly because it remains insoluble as the pH becomes very high.

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 a print is made on a photoconductive layer in which an image pattern of variations in electrical conductivity has been produced by exposure to light, the steps comprising placing the layer in contact with an aqueous electrolyte containing magnesium ions, passing electric current through the layer as cathode, distributed in accordance with said pattern to deposit magnesium hydroxide on the layer similarly distributed and applying to the magnesium hydroxide a reagent which forms a dye at the alkaline pH of the magnesium hydroxide.

2. A process according to claim 1 in which the electrolyte and reagent contain approximately neutral pH wetting agents.

3. A process according to claim 1 in which the reagent contains a diazonium salt and phloroglucinol.

4. In a photoconductographic process in which a print is made on a photoconductive layer in which an image pattern of variations in electrical conductivity has been produced by imagewise exposure to light, the steps comprising placing the layer in contact with an approximately

neutral aqueous electrolyte containing ions of a metal whose hydroxide is substantially insoluble and a material which is colorless at the pH of the electrolyte and turns into a colored dye at a higher pH, passing current through the layer distributed in accordance with said pattern with the layer as cathode to deposit the metal hydroxide at the conductive areas of said layer and to form and deposit said dye.

5. In a photoconductographic process the steps of electrolytically depositing on an imagewise exposed photoconductive layer as cathode, an image of magnesium hydroxide and applying to said image a reagent which forms a dye at the alkaline pH of the magnesium hydroxide.

References Cited in the file of this patent

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