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PHOTOCONDUCTOGRAPHY EMPLOYING MOLYBDENUM OR FERROUS OXIDE

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Fig. 1

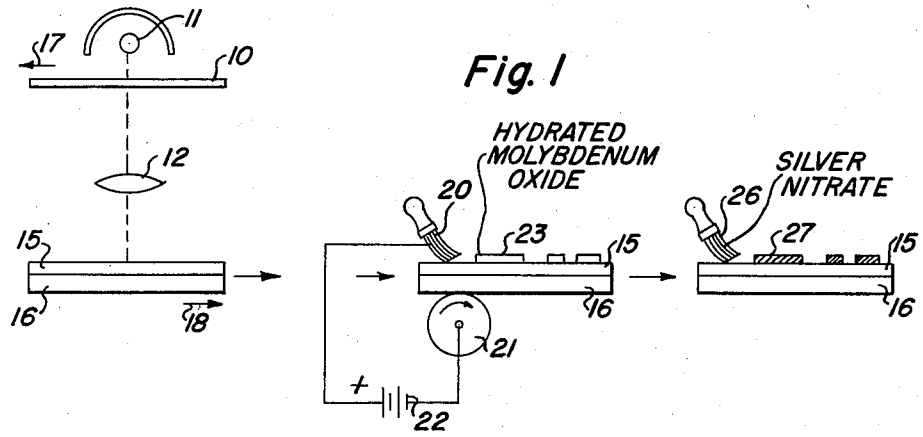
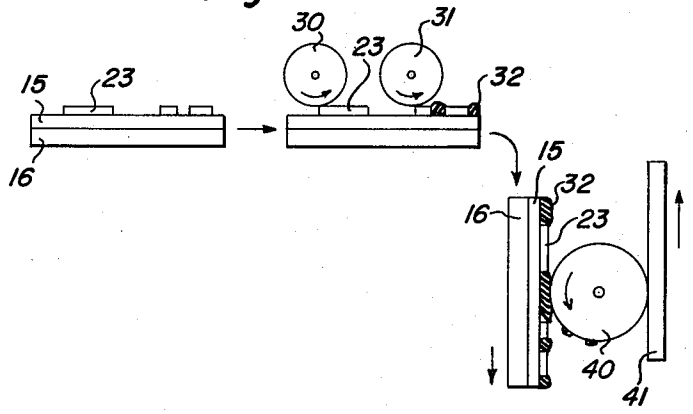


Fig. 2



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PHOTOCONDUCTOGRAPHY EMPLOYING MOLYBDENUM OR FERROUS OXIDE

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5 Claims. (Cl. 101—149.2)

This is a continuation-in-part of U.S. Serial No. 45,946, filed July 28, 1960.

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," 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 3,033,179.

Serial No. 45.943, Raymond F. Reithel, "Photoconductography Employing Spongy Hydroxide Images," and 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," and continuation-in-part Serial No. 271,412, filed April 8, 1963.

Serial No. 45,947, Raymond F. Reithel, "Photoconductography Employing Cobaltous or Nickelous Hydroxides," 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," 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. VanAllan, "Photoconductography Employing Quaternary Salts."

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 vonBronk and British 464,112 Goldmann modifications being described in British 789,309 Berchtold and Belgium 561,403 Johnson et al.

This invention relates particularly to photoconductography of the simple type in which a reducing agent is deposited as the image. Such photoconductographic processes are known, but prior to the present invention, they had relatively low photographic speed and gave relatively poor quality, i.e. low density, prints.

It is an object of the present invention to provide a photoconductographic process which has especially high recording speed. It is higher than any of the previous processes, particularly those in which a metal is deposited directly by the electrolytic action involved in photoconductography.

It is also an object of the invention to provide a process which attains higher densities at lower exposures than is possible with prior processes. The present invention provides the fastest pure photoconductographic process presently known.

It happens that this same invention when applied to lithography also gives excellent lithographic plates and again has higher photographic speed and better quality than prior processes.

According to the invention a photoconductographic image is deposited from a solution containing malybdic acid or ferrous sulfate or a combination of these. The image thus formed is faintly visible, if at all, but may be used to reduce a metallic salt such as silver nitrate to high optical density metal. The exact mechanism of the reducing properties of the plated hydrous oxide images is perhaps not fully understood. The following mechanism is proposed, but the invention gives the results stated whether or not this is the true theory involved. It is believed, for example, that the hydrous oxide of molybdenum existed in various states of valence deposited electrolytically and that these various valence states are good electron donors. From published scientific papers on the various reducing states of hydrous molybdenum oxide, it is evident that the molybdenum can exist in various states of valence which will differ mainly in the number of electrons with which it reacts at the cathode. In the case of the ferrous sulfate electrolyte, a hydrous ferrous oxide image is formed and the ferrous form is oxidized to the ferric state by an easily reducible metal ion such as that in silver nitrate.

Photoconductography involving molybdenum oxide or ferrous oxide images thus has the unique property of extremely high speed and utility as a control image, specifically a reducing image. These same images also have utility as hydrophilic images on a hydrophobic base for making litho plates. Thus the present invention is applicable both to direct photoconductography and to photoconductolithography. Other objects and advantages of the invention will be more fully apparent from the following description when read in connection with the accompanying drawing in which:

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

FIG. 2 is an alternative embodiment applied to lithography.

In FIG. 1 a transparency **10** is illuminated by a lamp **11** and is imaged by a lens **12** on a photoconductive zinc oxide layer **15** carried on a conducting support **16**. The transparency **10** moves to the left as indicated by the arrow **17** and the zinc oxide layer **15** moves synchronous-

ly with the image as indicated by the arrow 18. If the photoconductive layer is of the type which does not retain its charge in conductivity following exposure, it is developed during exposure. However, in the arrangement shown in FIG. 1, the image in the zinc oxide layer persists for a short time following exposure. The exposed photoconductive layer is then passed between electrodes consisting of brush 20 and a roller 21, the latter being the cathode and the potential difference being provided by a source indicated schematically at 22. The electrolyte contained in the brush 20 is a solution of molybdic acid. A slightly less preferred embodiment of the invention employs a solution of ferrous sulfate. In either case a hydrated oxide of the metal is deposited as an image 23 which is just faintly visible on the photoconductive layer 15. Thus in the most preferred embodiment of the invention, the image consists of hydrated molybdenum oxide. As mentioned above, the molybdenum is probably in various valence states.

The image is then passed under a brush 26 containing a solution of silver nitrate which is reduced by the hydrated molybdenum oxide to form a silver image 27 on or in the molybdenum oxide image.

The deposition of hydrous molybdenum oxide from an electrolyte containing molybdic acid requires only a very low intensity electric current and accordingly this process has an exceptionally high speed in terms of exposure required in the first step illustrated in FIG. 1.

In FIG. 2 the hydrated molybdenum oxide image 23 has been prepared in the same way as in FIG. 1 and with the same high photographic speed. However, it is used directly in a standard lithographic process as a litho plate, that is, the image 23 is wet by a fountain solution roller illustrated schematically at 30, the fountain solution being repelled by the hydrophobic zinc oxide-in-resin layer 15. The print then passes an inking roller 31 from which a greasy ink 32 is applied to the exposed areas of the hydrophobic zinc oxide but does not adhere to the image area 23. This greasy ink image 32 is then transferred to an offset drum 40 and thence printed onto a sheet of paper 41 all in the usual way.

Examples of the invention are as follows:

Example 1

As one example of the first embodiment, a dyed zinc oxide layer on conducting support was exposed imagewise to 15 ft. candle intensity for 1 second through a photographic step-wedge of density increments of 0.3. This conducting image was developed electrolytically using a viscose sponge brush electrode 20, held at 80 volts positive with respect to the zinc oxide layer, with a solution consisting of 0.8% molybdic acid, and two slow strokes development at ten seconds per stroke. A faint brown image was produced on the photoconductor surface. This image was further developed, chemically by bathing it with a 5% silver nitrate solution. A black image of reduced silver appeared in the form of, and relative to the amounts of, the hydrated molybdenum oxide image within one second after treatment. This image had a maximum density of 0.90 and a gamma of 0.48.

Example 2

A dye-sensitized zinc oxide layer on conducting support was exposed through an 0.3 density increment photographic stepwedge to an intensity of 400 ft. candle for 5 seconds. The conducting image was developed electrolytically, using a viscose sponge brush electrode 20, held at 80 volts positive with respect to the zinc oxide layer, and a solution of 1% ferrous sulfate (pentahydrate) with 10 strokes development at 1 stroke per second. A yellowish-grey image, probably of hydrated ferrous oxide, resulted on the photoconductor surface. This image was intensified chemically, by bathing it with a 5% solution of silver nitrate. A black image of reduced silver, in the form of and relative to the amount of the hydrated ferrous oxide image, appeared within one second after treatment with the reducible salt solution. In Examples 1 and 2, the silver nitrate may be replaced by any soluble silver salt such as silver acetate, silver lactate or silver sulfate.

Example 3

A sheet of photoconductive material (zinc oxide resin on metal foil) was exposed for 10 seconds to 15 ft. candle tungsten radiation incident upon a silver step tablet in contact with the photoconductive surface. Electroyltic development was carried out with a developer consisting of an aqueous solution of 1.0 percent, by weight, of ferrous chloride tetrahydrate. The surface of the print was rinsed, "wetted-out" and inked.

The electrolytic deposit formed in those regions which received 150 ft. candle seconds exposure were ink-repellent; only the unexposed areas, or those receiving less than 1 foot candle second of exposure were ink-receptive.

Example 4

A sheet of the photoconductive material was exposed but electrolytically developed with an aqueous solution of 0.5 percent ferrous sulfate heptahydrate and then rinsed, "wetted-out" and inked. The areas which were exposed for 150 ft. candle seconds repelled the ink, whereas the unexposed areas, or those exposed for less than 10 ft. candle seconds, held the ink. The percentage of ferrous sulfate is not critical and the variation in range of exposures shown in Examples 3 and 4 does not follow the percentage precisely but all such examples give useful results of course.

Example 5

A sheet of the photoconductive material was exposed and then electrolytically developed with an aqueous solution consisting of 1.0 percent, by weight, of molybdic acid (H_2MoO_4). The print surface was rinsed, "wetted-out" and inked. The area exposed to 150 ft. candle seconds repelled the ink, the areas which had received 5 ft. seconds or less, exposure held the ink.

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 voltage or at higher concentration 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 which ever 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 cobalt metal images) 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 given various examples of the invention and preferred arrangements thereof, it is pointed out that the invention is not limited to these specific examples but is of the scope of the appended claims.

I claim:

1. In a photoconductographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer, the steps of electrolytically depositing on the surface of said layer in accordance with said pattern a reducing agent selected from the group consisting of hydrated molybdenum oxide and hydrated ferrous oxide and applying to the imagewise distributed agent a solution of a soluble silver salt.

2. In a photoconductographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer, the steps of electrolytically depositing on the surface of said layer in accordance with said pattern, a hydrated oxide selected from the group consisting of hydrated molybdenum oxide and hydrated ferrous oxide.

3. The process according to claim 2 in which the surface of said photoconductive layer is hydrophobic, said image is wet, the area of the photoconductor not covered by said image is inked and litho prints are made therefrom.

4. The process according to claim 2 in which said image is wet with a solution of soluble silver salt.

5. A latent record comprising a photoconductive layer on a supporting sheet and, on the surface of the layer an image-wise distribution of a hydrated oxide selected from the group consisting of hydrated molybdenum oxide and hydrated ferrous oxide.

References Cited in the file of this patent

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3,011,963	Johnson et al.	Dec. 5, 1961

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