

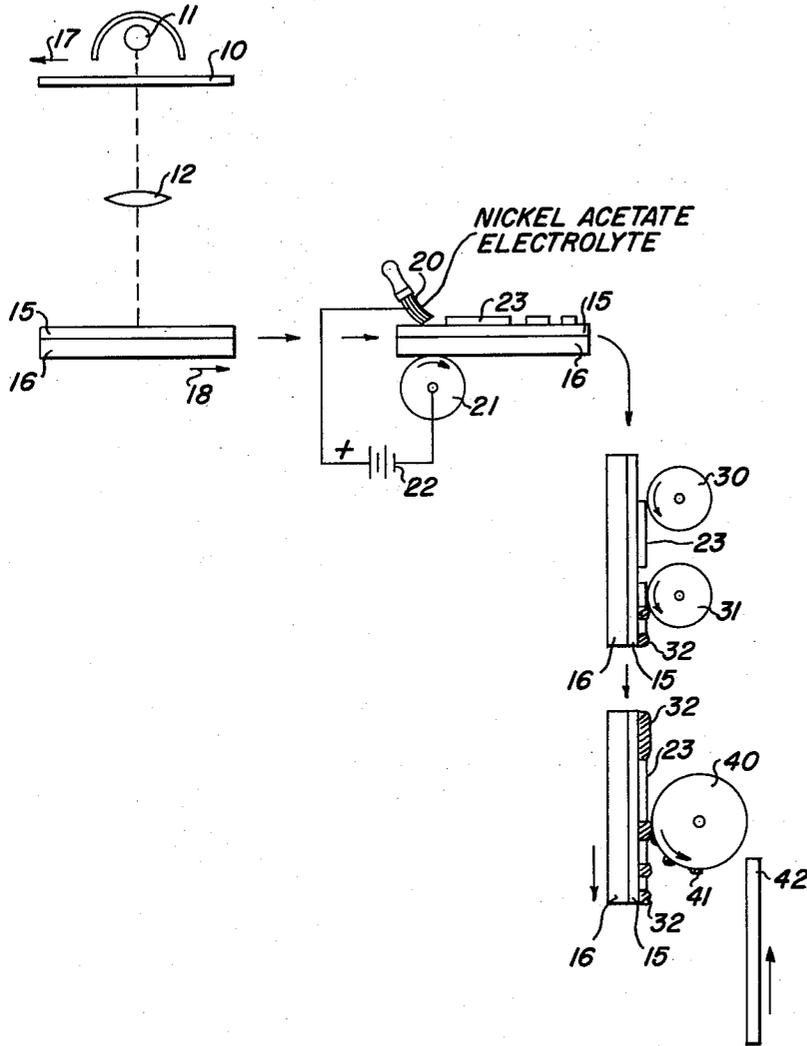
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PHOTOCONDUCTOLITHOGRAPHY EMPLOYING NICKEL SALTS

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PHOTOCONDUCTOLITHOGRAPHY EMPLOYING NICKEL SALTS

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This is a continuation-in-part of U.S. Serial No. 45,941, filed July 28, 1960, 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.

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

Serial No. 45,943, Raymond F. Reithel, "Photoconductography Employing Spongy Hydroxide Images," now abandoned 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. 45,947, 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 application 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 application Serial No. 120,037, filed June 27, 1961, now Patent No. 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 application 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 Patent No. 3,057,787.

Serial No. 45,954, John J. Sagura and James A. VanAllan, "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."

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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 photoconductolithography wherein a lithographic plate is made by photoconductographic methods.

The object of the present invention is to provide a much sturdier lithographic plate than has been produced by previous photoconductolithographic methods.

Another object of the invention is to provide a higher speed process for the manufacture of the litho plates.

The primary object of the invention is to give better quality prints than obtainable with plates made electrolytically from baths containing nickel ammonium sulfate. The improved quality appears as better contrast and better resolution.

According to the invention any of the standard photoconductographic methods may be used, except that the electrolytic development is from an electrolyte containing simple nickel ions. The photoconductographic image is nickel (nickelous is preferable to nickelic) hydroxide, which term includes hydrated oxides of nickel, and the image is deposited on a hydrophobic photoconductive layer such as the standard zinc oxide in resin binder. The electrolyte is a solution of nickel acetate, nickel lactate, nickel chloride or nickel sulfate—but not of a complex salt such as nickel ammonium sulfate since images produced from the latter do not give acceptable prints, apparently because the plates do not exhibit the required differences in hydrophilicity or hydrophobicity.

Thus nickel hydroxide is easily (as indicated by the high recording speed) deposited electrolytically and provides good discrimination in hydrophobicity between it and the zinc oxide in resin photoconductor. Also the litho plate thus made is quite rugged and several hundred high quality prints can be made from such a plate.

The invention itself will be more fully understood from the accompanying drawing which shows:

A schematic flow chart of a preferred embodiment of the invention.

In the drawing a transparency 10 illuminated by a light source 11 is focused by a lens 12 on a zinc oxide, resin, photoconductive layer 15 carried on a conductive support 16. Many such photoconductors are well known including those discussed in the above mentioned coiled applications. The transparency is moved to the left as indicated by the arrow 17 and the photoconductive layer is moved to the right synchronously with the image of the transparency, as indicated by the arrow 18. The zinc oxide layer retains temporarily the photoconductive image thus produced and this is electrolytically developed in a bath containing nickel acetate. This electrolyte is applied by a brush 20 as the exposed layer passes over a roller 21, the difference in potential between the brush 20 and roller 21 being provided by a D.C. source indicated schematically at 22. This deposits a nickel hydroxide image 23 which is hydrophilic. Since the zinc oxide layer 15 is hydrophobic the sheet constitutes a lithographic plate. A.C. potential may be used since the zinc oxide layer in contact with the electrolyte acts as a rectifier.

This plate is then lithographed by standard methods indicated schematically in the drawing. The fountain solution is applied by a wetting roller 30 to the hydrophilic

image 23. The plate is then inked with a greasy ink 32 by a roller 31. The ink adheres to the areas of the zinc oxide layer 15 which are not covered by the image 23.

The plate is then pressed against an offset drum 40 so that some of the ink 41 transfers thereto and in turn is transferred to a sheet of paper 42 in the usual way. All of this lithoprinting is conventional and is usually done on a standard office lithopress.

Examples of the invention are as follows:

Example 1

A sheet of the photoconductive material was exposed and electrolytically developed with an aqueous solution of 0.5 percent nickel acetate. The print was rinsed, "wetted-out" and hand inked. The area which had been exposed for 150 foot-candle-seconds repelled the ink, whereas the areas receiving less than 4 foot-candle-seconds held the ink. This Example 1 does not have as high contrast as the following examples, but the long scale obtained is of interest in connection with continuous tone lithography.

Examples 2, 3 and 4

Examples 2, 3 and 4 are similar to Example 1 except that nickel chloride, nickel sulfate and nickel lactate are respectively substituted for the nickel acetate and these give much higher contrast than Example 1. These three salts produce nickel hydroxide images which, on zinc oxide in resin, form excellent litho plates.

Example 5 is the same as Example 10 of my coiled application on spongy images, except that it is here employed as a litho plate. This example has sodium rhodizonate present with the nickel chloride in the electrolyte to raise the speed. It is still essentially nickel chloride electrolyte, but the image deposits more readily.

In my coiled application on low valence hydroxide images, e.g. nickelous, converted to higher valence hydroxide images, the nickelous hydroxide examples (and also the nickelic hydroxide examples) can be used according to the present invention as litho plates.

In exploring the special advantages of the simple nickel hydroxide images (and of the magnesium hydroxide, the molybdenum hydroxide, the manganese hydroxide alone or with iron, as litho plates all as discussed in my coiled application) over all prior and other known forms of photoconductolithography, many other materials were tried including zinc, aluminum, chromium and various other metal hydroxides mentioned in the coiled applications.

Specifically the nickel ammonium sulfate electrolyte and the following (lettered rather than numbered examples) all gave litho plates but all such plates were quite inferior in quality so much so that they would not be acceptable commercially. Prints from such plates had lower contrast and lower resolution than those using simple nickel, magnesium, molybdenum or manganese with iron.

(A) A sheet of the photoconductive material was exposed for 10 seconds to 1800 ft. candle tungsten radiation incident upon a high contrast positive transparency in contact with the photoconductive surface, and then was developed electrolytically with a viscose sponge wet with an aqueous solution containing 0.5 percent by weight zinc chloride. The sponge was held at a potential of 80 volts, positive, with respect to the aluminum foil electrode of the coating. After formation of the visible image, the print surface was rinsed with distilled water, "wetted-out" by application of a 1:7 water dilution of fountain solution and then was inked, by hand, with a plastic roller with Jet Halftone black offset ink.

The areas protected by the electrolytic deposit repelled the ink; the unprotected areas held the ink. Several transfer prints were made, by hand, from this master, by "wetting-out" and re-inking between each print. However, the exposures were relatively high and the contrast low.

(B) Another sheet of photoconductive material was ex-

posed for 10 seconds to a positive image obtained by opaque projection of an opaque, line-copy original (white areas yielding 5 ft. candle at exposure plane), and then electrolytically developed as in Example (A). The print surface was rinsed, and "wetted-out" as in the preceding example. When run on a No. 1250 multilith offset press, using 1:7 Repelex fountain solution and VanSon black No. 40904 ink, this master produced 100 prints but not of as good quality as by the present invention.

The optimum results with this (zinc) developer were obtained with zinc chloride concentrations between 0.25 and 1.0 percent.

(C) A sheet of the photoconductive material was exposed for 15 seconds to 1200 ft. candle tungsten radiation incident upon a silver step tablet in contact with the photoconductive surface, and then electrolytically developed, as in the preceding examples, with an aqueous solution containing 1.0 percent, by weight, chromic chloride hexahydrate and 4.0 percent, by weight, potassium oxalate monohydrate. The print surface was "wetted-out" with 1:7 Repelex and ink by hand with IPI Lithoday Jet Halftone Black offset ink. The areas which had received 18,000 ft. candle seconds exposure repelled the ink, whereas the areas receiving no exposure, or less than 560 ft. candle seconds, held the ink.

It has been found that the addition of salts other than potassium oxalate, i.e., potassium sulfate, to the aluminum or chromium salt developers, not only enhances the hydrophilic properties of the deposits but with these additions, the exposure required to produce an adequate degree of hydrophilicity is much lower.

(D) This was similar to Example A above but aluminum chloride was substituted for the zinc chloride. These examples A, B, C and D even with the additives mentioned gave litho plates of inferior printing quality compared to simple nickel, magnesium molybdenum and manganese hydroxides.

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 concentrations 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 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, so that either metal or hydroxide images are useful.

Having given examples of the invention and preferred embodiments 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 photoconductolithographic process in which an image pattern of variations in electrical conductivity is produced in a photoconductive layer the steps comprising placing the layer as a cathode in contact with an electrolyte containing in solution not more than 3% of a simple nickel salt selected from the group consisting of nickel acetate, nickel chloride, nickel lactate and nickel sulfate, applying a voltage greater than 30 volts between said cathode layer and an anode also in contact with the electrolyte to cathodically deposit on the layer a hydrophilic image consisting essentially of nickel hydroxide and lithoprinting from the layer and hydrophilic image.

2. The process according to claim 1 in which the photoconductive layer is zinc oxide in resin binder.

3. A lithographic plate comprising a flexible support, a hydrophobic coating of zinc oxide in resin on said support and a hydrophilic image pattern of nickel hydroxide on the surface of said coating.

References Cited in the file of this patent

UNITED STATES PATENTS

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