

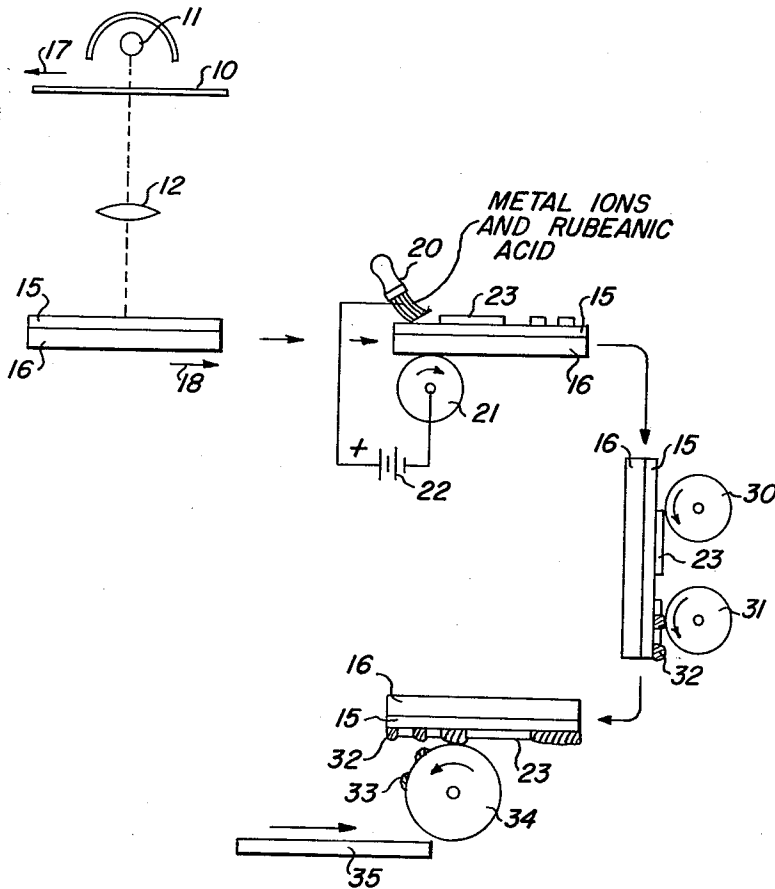
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PHOTOCONDUCTOLITHOGRAPHY EMPLOYING RUBEANATES

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## PHOTOCONDUCTOLITHOGRAPHY EMPLOYING RUBEANATES

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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.

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," 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," continuation-in-part Serial No. 120,036, filed June 27, 1961.

Serial No. 45,947, Raymond F. Reithel, "Photoconductography Employing Cobaltous or Nickelous Hydroxide," 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," 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 F. Sagura, "Photoconductography Employing Alkaline Dye Formation."

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. 45,959, 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 Von Bronk 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 in which a hydrophilic image is deposited electrolytically on a hydrophobic photoconductor such as zinc oxide in resin.

The object of the present invention is to provide a process of photoconductolithography which requires much smaller exposures than prior processes. Photoconductors have a sensitivity depending on the material used and on sensitizing by dyes and the like. For any one sensitivity, however, the amount of exposure required depends on the development step since some electrolytes deposit images of adequate "contrast" with less difference in current values between the exposed and unexposed areas of the photoconductor.

It is also an object of the invention to provide a lithographic plate having more strongly hydrophilic areas than prior photoconductolithographic plates. This results in the final litho prints having higher contrast.

One embodiment of the invention provides particularly rugged images so that a very large number of litho prints can be pulled from a single plate.

According to the invention the electrolytic step in a photoconductographic process employs an electrolyte containing rubeanic acid, i.e. dithiooximide, and a metal ion selected from the group consisting of iron, copper, nickel and cobalt. The copper, nickel or cobalt form a metal rubeanate directly, which tends to polymerize, thus becoming particularly rugged so that a large number of litho prints may be pulled therefrom. The rubeanate remains hydrophilic however. In the case of iron the deposit is a complex compound of iron and rubeanate but it is not believed to be simply iron rubeanate. It is not known exactly what form the compound takes. Nevertheless, it does deposit readily, so that it requires less exposure of the photoconductive layer to produce the necessary conductivity. Furthermore the slightly acid developing solution containing iron ions is more stable than the other three species. The iron complex of rubeanate is the most hydrophilic of the four.

The invention 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 lamp 11 is focused by a lens 12 on a zinc oxide in resin photoconductive layer 15 carried on a conducting support 16. The transparency 10 is moved as indicated by the arrow 17 and the photoconductive layer 15 is moved synchronously with the image of the transparency as indicated by arrow 18. The present process could also be used with photoconductive processes in which the development is performed simultaneously with the exposure, but in the arrangement shown, development takes place following exposure.

The conductivity image which persists in the zinc oxide layer 15 is electrolytically developed by a brush 20 containing the metal ion and rubeanic acid and by a counter electrode 21, the difference in potential being supplied by a source indicated schematically at 22. An A.C. source could be used since the photoconductor 15 or the interface between it and the electrolyte, acts as a rectifier so that the photoconductor is the cathode. This is normally true for all photoconductographic processes employing zinc oxide in resin. The image 23 of metal rubeanate is then moistened with a fountain solution by the usual moistening roller of litho printing indicated schematically at 30. Greasy ink is then applied by a roller 31 and deposits at 32 on the unexposed areas of the zinc oxide, resin, layer. Part of the ink 32 transfers, as shown at 33

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to an off-set drum 34 and in turn is printed on a sheet of paper 35 in the usual way.

Standard lithographic presses used in offices are quite satisfactory for this purpose.

#### Example 1

In one example of this invention, a sheet of photoconductive material, consisting of dye-sensitized zinc oxide in a resinous binder coated on an aluminum-foil-paper-laminate, was exposed for 10 seconds to 400 ft. candle tungsten radiation incident upon a silver step tablet in contact with the photoconductive surface, and then was brush developed with a viscose sponge wet with a solution made up by mixing 50 ml. of a one-percent aqueous solution of ferrous chloride tetrahydrate with 20 ml. of ethyl alcohol in which was dissolved 0.2 gram of dithiooximide, (rubeanic acid). The sponge was held at a potential of 80 volts, positive, with respect to the aluminum foil support for the coating. After formation of the barely visible image, the surface was wetted with 1:7 water dilution of commercial fountain solution, then was inked with a plastic roller using standard offset ink (Jet Half-tone Black). The areas of the photoconductive surface which had received exposure greater than 20 ft. candle repelled the ink but the unexposed areas, specifically those receiving less than 20 ft. candle seconds were found to be ink receptive. Good quality prints were pulled from the plate. As pointed out above, it is not known what form the iron-rubeanate complex compound of the image takes.

#### Example 2

The same processing as in Example 1 was applied to a similar photoconductive material which had been exposed for only one second to only 40 ft. candle tungsten illumination (i.e. one-hundredth of the previous exposure). An even better litho plate was obtained in this second example which indicates that the process is quite fast. Since the exposure in Example 1 corresponds roughly to the fastest used with prior photoconductolithographic processes, the present process appears to be at least 100 times faster than said prior processes. When run in a standard offset lithographic press (Addressograph Multigraph Model 1250) the printing master of this second example produced 500 high quality ink copies.

#### Examples 3, 4, 5

These examples are substantially the same as Example 2 (and 1) except that soluble copper, cobalt or nickel salts were substituted for the ferrous chloride tetrahydrate. The optimum exposure in these cases was slightly greater than in Example 2 but less than in Example 1. Furthermore, the inherent polymerization of the copper, cobalt or nickel rubeanates made the plates more rugged and more than 500 prints were obtainable from such plates.

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In the coiled application by Reithel entitled Photoconductolithography Employing Magnesium Salts, the hydrophilicity of magnesium hydroxide is discussed. I have found that aluminum hydroxide operates similarly.

For example, if the brush 20 in the accompanying drawing contains an electrolyte consisting of 1 g. of aluminum chloride hexahydrate and 4 g. of ammonium chloride in 50 cc. of distilled water, the image 23 is aluminum hydroxide or hydrated oxide which is hydrophilic and the plate is ready for litho printing. Actually such a system requires somewhat greater exposures and the difference in hydrophobicity of the aluminum hydroxide and the background of zinc oxide (in resin) is not as great as for the rubeanates.

However, the aluminum hydroxide image need not be used for litho printing, but is very useful if a lake forming dye is applied thereto. This may be applied after the image is deposited, but preferably for the sake of simplicity, it is incorporated in the electrolyte so that the lake is formed as the aluminum hydroxide is deposited. In the aluminum hydroxide example just given, 50 cc. of distilled water containing 2 g. of sodium alizarin sulfonate was added to the 50 cc. of aluminum chloride solution. The spongy image deposited in this case was an aluminum hydroxide lake which is highly colored and constituted an acceptable photoconductographic print directly.

Having thus described preferred embodiments of the invention it is pointed out that it is not limited thereto but is of the scope of the appended claims.

I claim:

1. In a photoconductolithographic process, the steps of depositing on a hydrophobic photoconductive surface from an electrolyte containing rubeanic acid and metal ions selected from the group consisting of iron, copper, nickel and cobalt, an image of the compound of said metal and rubeanate which image is hydrophilic and litho printing from said surface and image.

2. The process according to claim 1 in which the metal ions are selected from the group consisting of copper, nickel and cobalt whereby the image is polymerized metal rubeanate.

3. The process according to claim 1 in which the metal ions are iron whereby the image is an iron complex of rubeanate which is more hydrophilic than copper, nickel and cobalt rubeanates.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

|           |                 |               |
|-----------|-----------------|---------------|
| 748,609   | Hunt            | Jan. 5, 1904  |
| 2,485,678 | Tribble         | Oct. 25, 1949 |
| 2,719,481 | Brotthof et al. | Oct. 4, 1955  |
| 2,794,388 | Lake et al.     | June 4, 1957  |