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D. R. EASTMAN ETAL

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ELECTROLYTIC RECORDING WITH ORGANIC POLYMERS

Filed July 28, 1960

Fig. 1



Fig. 2

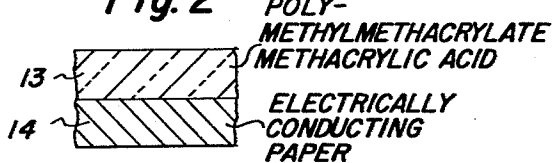


Fig. 3

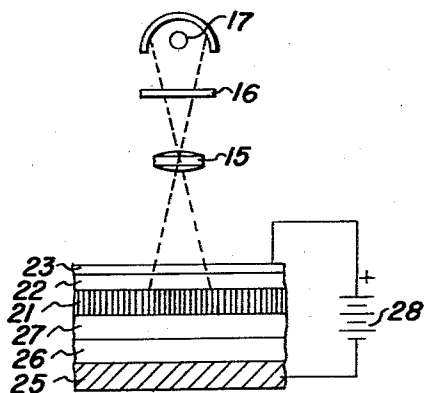


Fig. 4

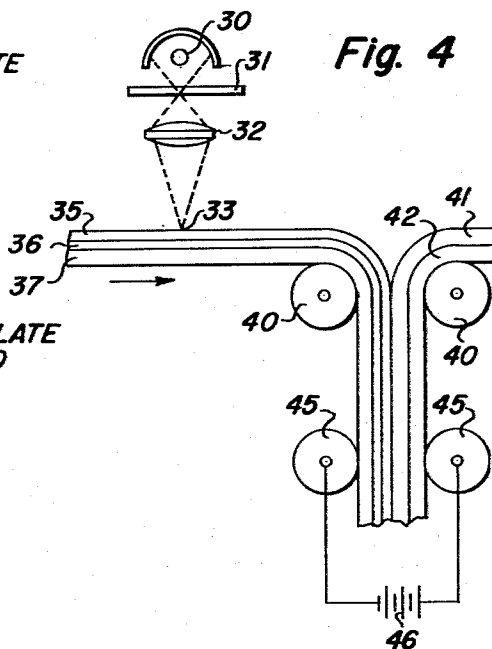
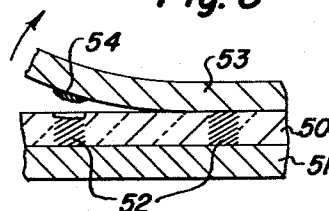


Fig. 5



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ELECTROLYTIC RECORDING WITH ORGANIC POLYMERS

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9 Claims. (Cl. 101—149.1)

This invention relates to electrolytic recording, particularly to such recording for 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 moment produces only a uniform dot. The present invention is an improved form of the electrolytic recording system described in copending application Serial No. 46,034, filed concurrently herewith by F. Urbach and D. Pearlman. Cross reference is also made to the following series of cofiled 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 J. 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. 45,958, Donald R. Eastman, "Photoconductolithography Employing Rubeanates."

Electrolytic facsimile systems are well known. Electrolytic photoconductography is described in detail in British Patent 188,030 Von Bronk and British Patent 464,112 Goldmann, modifications being described in British Patent 789,309 Berchtold and Belgian Patent 561,403 Johnson et al. The various chemical reactions used in electrolytic facsimile and electrolytic photoconductography include metal deposition, dye formation and deposition, metal or dye bleaching, the activation of photographic plates and the formation of minute bubbles of gas by the passage of electric current.

The present invention has many of the advantages of the Urbach and Pearlman system just referred to. For example it permits use of any of a large number of dyes or pigments for color. It is particularly useful in the production of lithographic printing masters or of transfer masters from which several prints may be pulled. The present invention produces positives directly when used in photoconductography. It has the advantage over the use of gelatin as described by Urbach and Pearlman, that the resulting master print or printing plate is more rugged and more uniform.

In the present invention the electric current produced by facsimile or preferably by the effect of light on a photoconductive layer is passed through a layer of a slightly water permeable but not water soluble synthetic polymer in the presence of sufficient ionic materials to make the layer electrically conductive. Preferably the layer consists of cellulose acetate phthalate or a copolymer of methylmethacrylate and methacrylic acid. Such materials are softened or made more soluble by the passage of current and the distribution of solubility in the layer will correspond to the pattern of the current flow.

The change in solubility is, of course, relative to some particular solvent or group of solvents. Water is the solvent in which the solubility of each of the materials mentioned changes. With such a solvent present in the layer, a record is made by any one of a number of systems. The solvent may be used to wash off the more soluble areas leaving the remaining areas as a relief for inhibition printing or for relief printing, intaglio printing or litho printing to the extent that the layer has a hydrophilicity different from that of the exposed base. The whole of the layer may be dyed or only the more soluble parts may be dyed and in either case these more soluble parts may be transferred to a receiving sheet and with the above specified materials it is possible to obtain several satisfactory transfer prints from this latter method. Also the plate, because of differences in hydrophilicity corresponding to the differences in solubility, may be used directly for litho printing without washing off any of the layer. In any of the embodiments, additional materials may be included in the polymer to improve the electrical conductivity, the acceptance or rejection of dyes or inks and the solubility of the layer before the passage of electric current therethrough.

The invention is particularly useful with ferrography in which a relief image contains magnetized material which attracts magnetic ink.

Although the reason is not understood, we have found it possible to soften these polymer layers by the passage of electric current in either direction through the layer.

Other objects and advantages of the invention will be apparent from the following description and examples when read in connection with the accompanying drawings in which:

FIG. 1 is an enlarged cross section of one embodiment of the invention.

FIG. 2 similarly shows another embodiment of the invention.

FIG. 3 schematically illustrates the application of the invention to one form of photoconductography.

FIG. 4 similarly shows the application to another form of photoconductography.

FIG. 5 illustrates application of the invention to transfer printing.

In FIG. 1 a current responsive layer 10 of cellulose acetate phthalate is coated on a conducting support consisting of a metal foil 11 and a paper back 12. In FIG. 2 a current responsive layer 13 consists of poly(methyl-methacrylate-methacrylic acid) coated on an electrically conducting paper 14. Either current sensitive material may be coated on either form of conducting support.

As an example of an electrically conducting paper 14 (not using a metal foil laminate such as 11 and 12), a high wet strength paper weighing about 8.9 pounds per 100 square feet was sized with the following solution:

1½ g. potassium chloride
2 cc. formalin
8 cc. glycerol
200 g. of a solution containing 6% gelatin in water.

The pH of the solution was adjusted to 4.5 with hydrochloric acid.

On this paper was coated a solution made by adding 0.2 g. Grasol Fast Black G (Geigy) to 10 cc. of a solution containing 15% by weight of cellulose acetate phthalate in ethyl alcohol and methyl cellosolve mixture. The coating was 0.002 inch thick (wet).

This coating when dried down forms the electrically sensitive layer of cellulose acetate phthalate. As a second example, poly(methyl-methacrylate-methacrylic acid), was similarly dissolved in ethyl alcohol and similarly coated on the above high wet strength paper. This example is the one illustrated in FIG. 2.

As shown in FIG. 3, a photoelectrode consisting of a transparent electrode 23, a photoconductive layer 22 and a unidimensionally conducting layer 21 is positioned to receive a light image of a transparency 16. The image is produced by a light source 17 and a lens 15 and is focused on the photoconductive layer 22 through the semi-transparent electrode 23. The unidimensional conductor 21 is similar to that described in British Patent 789,309 mentioned above and was made by winding enamelled copper wire 0.004 inch in diameter as a coil impregnated during winding with an epoxy resin. After hardening of the resin the coil was sliced radially to produce a thin sheet of resin having copper wires extending through the sheet and perpendicular to the surface. The surface of this unidimensional conductor 21 (it does not conduct sideways) was coated with a cadmium sulfide photoconductor in a resinous binder 22 and, after drying, the photoconductor was overcoated, by evaporation, with a thin transparent gold electrode 23. Silver paste applied around the edge of the evaporated gold layer provides means for electric contact. The three layers 21, 22, 23 together constitute a photoelectrode which is placed in good electric contact with the recording layer 27. To enhance the conductivity of the base 26, it is preferably moistened with an electrolyte such as 10 cc. glycerin, 4 g. potassium chloride and 100 cc. water. A counter electrode 25 of metal is placed in contact with the back of the conducting support 26 and a potential of 57 volts is applied between the transparent gold electrode 23 and the counter electrode 25 by means of a source 28 of potential. Voltages between 10 volts and 100 volts give satisfactory results with this particular arrangement. The actual voltage is not critical but higher speeds are obtainable with higher voltages up to the point where it causes breakdown or sparking.

The recording layer 27 and its support 26 are then removed from the exposure sandwich and a record is formed in or by the layer 27 by any one of a number of systems depending on the pattern of solubility in the layer.

For example the layer is water soluble and in a stream of warm water, the more soluble areas wash off leaving a relief image. If the layer 27 is dyed before or after washing off the more soluble areas, the resultant relief constitutes a record itself or can be used for imbibition printing or as a printing plate. Alternatively the layer may simply be dyed so that the more soluble areas absorb more dye and are darker than the less soluble areas.

Unusually high quality litho prints are obtained without the wash off step merely by applying water to the layer so that the water is absorbed in the areas through which current has passed and not appreciably absorbed in the areas through which current has not passed. A greasy ink is then applied to the latter area and is printed directly or by offset onto paper in the usual way.

In the arrangement shown in FIG. 4 light from a lamp 30 illuminates an elongated area transverse to an original 31 which is moved in front of the source 30. An image of the illuminated area is formed by a lens 32 at the point 33 past which a photosensitive sheet is passed synchronously with the moving image. The photosensitive sheet consists of a zinc oxide (in binder) layer 35 coated on a metal foil 36 and supported by a paper port 37. Zinc oxide has the property of temporarily retaining the increase in conductivity. Hence the increase in conductivity continues for a short time after the exposure. The layer 35 is then pressed by rollers 40 into contact with a current sensitive recording layer 41 carried on a conducting support 42. The two sheets are then passed between roller electrodes 45, one of which contacts the edge of the metal layer 36 and the other of which contacts the back of the conducting paper support 42. Current supplied by a power source 46 flows through the areas of the zinc oxide 35 which have just previously been exposed and through the corresponding areas of the recording layer 41 to change the solubility of the latter. The layer 41 is then ready for the production of a record by any one of the various systems involving the presence of water in the layer 41, and its differential solubility. The present invention is particularly useful in transfer printing as illustrated in FIG. 5 in which the layer 50 carried on a support 51 has been treated by the passage of electric current distributed in an imagewise pattern so that the shaded areas 52 have been rendered more water soluble than the remaining areas of the layer 50 and hence the areas 52 are relatively soft. These areas readily transfer to a sheet of paper 53 pressed into contact with the layer 50 and then stripped therefrom carrying some of the soluble areas 52 to form an image 54 on the paper 53. This image 54 may already be colored when it is transferred or may be subsequently treated to provide a contrast with the paper support 53 in color or in hydrophilicity if this transfer image is to constitute a lithographic plate.

An example in which this electrolytic softening of a polymer is employed in ferrography is as follows:

3 g. of (ferromagnetic) $\gamma\text{Fe}_2\text{O}_3$ was added to 70 cc. of ethyl alcohol and 30 cc. of ethyl alcohol in which was dissolved 3 g. of MMAX (methylmethacrylate-methacrylic acid). The mixture was blended by rolling in a pint-size ceramic container containing 12 ceramic balls for 56 hours.

A thin (0.003 in. wet) layer of the mixture was coated on a KCl-gelatin sized, ferrotyped conducting support, application being made on the ferrotyped surface.

The sizing solution contained 1.5 g. KCl, 2 cc. 40% formaldehyde, 8 cc. glycerol in 200 g. of 6%, by weight, gelatin with pH adjusted to 4.5 with HCl.

The backing of the above recording layer was moistened with a 0.5%, by weight, KCl solution and an aluminum foil counter-electrode applied to this same surface. The coated surface of this sandwich was then placed, under pressure, in contact with the unidirectional layer of a reusable photoelectrode.

During a 20 sec. imagewise illumination of the photo-

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conductive surface of the photoelectrode, a 70 v. D.C. potential was applied between the aluminum foil counter-electrode and the conducting transparent electrode of the photoelectrode.

In the illuminated areas, corresponding to the areas of highest current flow, the polymer layer was rendered soluble. These solubilized areas were then removed by rinsing in 120° F. water.

The recording sheet was air dried, and the image material magnetized by drawing several times across one pole of a bar magnet. The sheet was bathed in a carbonyl iron-Freon 113 slurry, and the iron which was attracted to the $\gamma\text{Fe}_2\text{O}_3$ image was transferred by means of a pressure roller to a sheet of paper.

In another example the above results are obtained by incorporating ferromagnetic Fe_3O_4 in the MMAX recording layer in place of the Fe_2O_3 . Any of the hard (magnetically hard) ferromagnetic materials which can be finely divided, including the nickel iron compounds used in permanent magnets, produce excellent results.

The ferromagnetic material may be magnetized before electrolytic hardening, after the hardening and before washing off the softer areas or after the washing off is complete. A colored magnetic material (ink or toner powder) is applied to and printed (transferred) from the magnetized areas.

Having thus described several of the very successful examples of our invention, we wish to point out that it is not limited to the specific arrangements shown but is of the scope of the appended claims.

We claim:

1. An electric current responsive sheet comprising an electrically conducting flexible base and a thin coating between .001 and .01 inch thick when wet on the flexible base, said coating being a slightly water permeable but not water soluble, polymer selected from the group consisting of cellulose acetate phthalate and poly(methylmethacrylate-methacrylic acid).

2. A current responsive sheet according to claim 1 in which the electrically conducting flexible base consists of water permeable paper with a pH less than 6.0 containing an ionic salt.

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3. A current responsive sheet according to claim 1 in which said polymer contains in suspension a magnetically hard ferromagnetic material.

4. A method of recording an image which comprises creating a pattern of electric current corresponding to said image, passing said current through an electrically conducting layer of a slightly water permeable but not water soluble polymer selected from the group consisting of cellulose acetate phthalate and poly(methylmethacrylate-methacrylic acid), to increase in accordance with said pattern the solubility of the layer in water, and in the presence of water in the layer, forming a record in accordance with the differences in solubility of the layer caused by the passage of current.

5. The method according to claim 4 in which said forming a record consists of applying to and transferring from the less soluble areas of the record, a greasy ink.

6. The method according to claim 4 in which said forming a record consists of applying to and transferring from the more soluble areas of the record, an aqueous solution of dye.

7. The method according to claim 4 in which said forming a record comprises washing off the more soluble areas of the record and applying a dye to the remaining areas.

8. The method according to claim 4 in which said forming a record comprises pressing against the layer a receiving sheet to which only the more soluble areas adhere and transfer.

9. The method according to claim 4 in which the polymer contains a magnetically hard ferromagnetic material and in which said forming a record comprises washing off the more soluble areas of the record, and with the ferromagnetic material in a magnetized state, applying a colored magnetic material to the remaining areas.

References Cited in the file of this patent

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2,294,149	Kline et al.	Aug. 25, 1942
2,381,704	Terry	Aug. 7, 1945
2,555,321	Dalton et al.	June 5, 1951

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,106,155

October 8, 1963

Donald R. Eastman et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 17, for "100" read -- 1000 --; column 4, line 23, for "port 37" read -- support 37 --; line 60, for "The" read -- This --.

Signed and sealed this 14th day of April 1964.

(SEAL)

Attest:

ERNEST W. SWIDER

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