United States Patent Office 3,285,837 Patented Nov. 15, 1966

3,285,837

ELECTROLYTIC DEVELOPMENT PROCESS FOR PHOTOCONDUCTIVE COPYSHEETS

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No Drawing. Filed Jan. 9, 1963, Ser. No. 250,226
15 Claims. (Cl. 204—18)

This invention relates to an image recording process. In one aspect, the invention relates to a novel electrolytic development technique for photoconductive copysheets. In another aspect, the invention relates to the information of visible dye images on the surface of light exposed photoconductive copysheets.

In one method for developing permanent visible images on photoconductive copysheets, the copysheet is exposed to a light image, then developed electrolytically to deposit a metallic or other visibly distinct material on the more conductive areas of the copysheet surface. Such a process is described in United States Letters Patent 3,010,883. Suitable photoconductive copysheets are also disclosed in United States Letters Patent 3,010,884. In general, the copysheets comprise a photoconductive powder, such as zinc oxide, bonded to a contiguous electrically conductive backing, usually by an electrically insulative binder. If the electrically conductive backing of the photoconductive copysheet is connected as the anode, it has been found that a rectification effect substantially reduces current passage and makes the electrolytic development difficult. This rectification effect is not observed when the electrically conductive backing is connected as the cathode, which is therefore the procedure usually employed. However, cathodic electrolytic development generally restricts the developer materials to those which are reduced at the cathode, e.g. silver ions to free silver, etc. Many extremely useful oxidizable compounds and materials bearing a net negative charge have therefore not been practically useful in the electrolytic development of light exposed photoconductive copysheets.

In my copending patent application, United States Serial No. 820,254, filed June 15, 1959, now U.S. Patent No. 3,127,331, a method for eliminating the abovementioned rectification effect is disclosed. This method involves cathodic electrolytic deposition of a free metal on the more conductive portions of the exposed photoconductive sheet, then carrying out another electrolytic reaction with the photoconductive sheet connected as the anode. The presence of the free metal deposit destroys the rectification barrier and permits current passage in both directions through the photoconductive copysheet. The anodic electrolytic development permits the use of such developers as the leuco form of vat dyestuffs and various colored anions, the latter being exemplified by acid type dyestuffs. However, this technique does require two distinct electrolytic steps.

It is therefore an object of this invention to provide a new method for electrolytic development of photoconductive copysheets.

Another object of this invention is to provide a method for cathodic electrolytic development of photoconductive copysheets using negatively charged developer materials.

A further object of this invention is to provide a method for electrolytic development of photoconductive copysheets in a single step using negatively charged developer materials.

Still another object of this invention is to provide photoconductive copysheets having visible image deposits thereon.

Various other objects and advantages will become apparent from the following disclosure.

In accordance with this invention, it has been found that water soluble anionic dyes, i.e. dyes having a negatively charged chromophore, can be electrolytically deposited from solution onto a cathodically connected photoconductive copysheet, provided the solution also contains a polyvalent metal ion. The water soluble acid dyes, generally in the form of their sodium or potassium salt, are particularly suitable, the non-mordant acid dyes being preferred. Such acid dyes are generally sulfonic acids of compounds in the nitrophenol, azo, triphenylmethane, anthraquinone, indigoid and other series, the majority being azo, (including polyazo) and anthraquinone dyes. Reactive acid dyes, which contain reactive chlorine that is converted to hydroxyl in alkaline media, e.g. Procion, Cibacron, Drimarene dyes, etc. may be employed. Other reactive dyes include the Remazol and Reactone types. The polyvalent metal ion must, of course, not precipitate or insolubilize the colored anion in the aqueous developer solution. Polyvalent metals selected from Group II of the Periodic Table, particularly magnesium, calcium and zinc, and metals of Group VIII, particularly nickel, are especially preferred, and the use of both magnesium and nickel has provided outstanding results. Water soluble salts of the polyvalent metal ions, e.g. chlorides, nitrates, sulfates, acetates, etc., may be added to the aqueous bath to provide the polyvalent metal ions.

The actual mechanism by which the water soluble anions are carried to the cathode is not fully understood. When the polyvalent metal ion is not present, the negatively charged dye ions migrate to the positively charged electrode or anode. Since the dyes employed are water soluble, electrophoresis does not seem to be involved. Moreover, complex formation does not appear to be consistent with the experimental data. Whatever the explanation, addition of the polyvalent metal containing ion causes deposition of the dye at the cathode, thereby producing vivid, high contrast, developed images on the photoconductive copysheet surface in a single electrolytic development step without any rectification barrier.

The aqueous developer solutions are generally prepared with up to about one percent by weight of the water soluble dye and from about 1 to about 5 percent by weight of a metal salt to provide the polyvalent metal containing cation. The dye is preferably first dissolved in the water followed by addition of the metal salt. Various positively charged latex or emulsions particles which are not coagulated by the other constitutents of the developer may also be incorporated into the developer solution. Such latices having positively charged particles, e.g. copolymers of vinyl chloride and vinyl acetate, tend to increase the contrast of the resulting prints. Examples of illustrative aqueous developer solutions which have been used to develop visible images on photoconductive zinc oxide copysheets are as follows:

Example 1

1% Patent Blue A (C.I. 42080)
3% $MgCl_2 \cdot 6H_2O$
0.5% $NiCl_2 \cdot 6H_2O$

Example 2

1% Pontacyl Fast Violet VR (C.I. 45190)
3% Magnesium acetate
0.5% $NiCl_2 \cdot 6H_2O$
3% sodium acetate

Example 3

1% Cibacron Turquoise Blue G
2.5% $NiNO_3 \cdot 6H_2O$

Example 4

1% Drimarene Black Z-BL
2.5% $NiNO_3 \cdot 6H_2O$

Example 5

1% Xylene Milling Blue BC (C.I. 42645)
3% $MgCl_2 \cdot 6H_2O$
0.5% $NiCl_2 \cdot 6H_2O$
50% ethanol
45.5% water

Other suitable dyes which have been used in the above-mentioned manner are Chlorantine Fast Turquoise VLL (C.I. 74180), Chlorantine Fast Yellow 4GLL (C.I. 29000), Alizarin Cyanine Green G-CF (C.I. 61570), Basolan Chrome Brilliant Red 3BM (C.I. 45305), Nigrosine B (C.I. 50420), Pontacyl Violet C4BN (C.I. 42650), Alizarin Rubinol 3G-CF (C.I. 68205), Pontamine Sky Blue 6BX (C.I. 24410), duPont Paper Yellow (C.I. 10316), Cibacron Brown 3GR, Cibacron Violet 2R, Cibacron Brilliant Red 3B, Drimarene Red Z-2B, Drimarene Blue Z-RL, Drimarene Black Z-BL, Alizarin Red S (C.I. 58005), and Indigotine. Particularly useful combinations of polyvalent metal and water soluble anionic dye are set forth in Table I.

TABLE I

Color Index Index	Acid Dyestuff	Polyvalent Metal Ion
47005	Quinoline Yellow	Ni+Mg
10316	Paper Yellow L	Ni+Mg
18965	Pontacyl Light Yellow GX	Ni+Mg
24410	Pontamine Sky Blue 6BX	Ni+Mg
10316	Napthol Yellow S	Ni
13065	Metanil Yellow conc	Ni+Mg
34010	Pontamine Diazo Blue NA conc	Ni+Mg
43830	Pontachrome Azure Blue B conc	Ni+Mg
43820	Pontachrome Blue ECR	Ni+Mg
63010	Anthraquinone Blue BN	Ni+Mg
42085	Pontacyl Green B6 ex. conc	Ni+Mg
42080	Pontacyl Brilliant Blue A conc	Ni+Mg
42650	Pontacyl Violet C4BN	Ni+Mg
27290	Crocein Scarlet N ex	Ni+Mg
24410	Pontamine Sky Blue Greenish conc	Ni+Mg
24340	Pontamine Brilliant Blue G conc	Ni+Mg
29160	Pontamine Test Scarlet 4BS	Ni+Mg
28395	Pontamine Test Rubine B conc	Ni+Mg
	Drimarene Scarlet Z-GL	Ni+Mg
	Drimarene Navy Z-2RL	Ni+Mg
	Drimarene Golden Yellow Z-R	Ni+Mg
	Drimarene Yellow Z-3GL	Ni+Mg
	Drimarene Yellow Z-5GL	Ni+Mg
	Drimarene Turquoise Z-G	Ni+Mg
	Drimarene Violet Z-RL	Ni+Mg
	Drimarene Black Z-BL	Ni+Mg
	Drimarene Red Z-RL	Ni+Mg
	Drimarene Red Z-2B	Ni+Mg
	Drimarene Blue Z-RL	Ni+Mg
	Cibacron Yellow R	Ni+Mg
	Cibacron Brilliant Yellow 3G	Ni+Mg
	Cibacron Rubine R	Ni+Mg
	Cibacron Blue 3G	Ni+Mg
	Cibacron Orange (Brilliant) GP	Ni+Mg
	Cibacron Brilliant Red B	Ni+Mg
	Cibacron Brilliant Blue BR	Ni+Mg
	Cibacron Turquoise Blue G	Zn
	Cibacron Yellow G	Ni+Mg
	Cibacron Brilliant Violet ZR	Ni+Mg
	Cibacron Brilliant Red 3B	Ni+Mg
58005	Alizarin Red S	Mn
58005	Alizarin Red S	Ni
58005	Alizarin Red S	Zn
	Chlorantine Fast Turquoise VLL	Zn+Ni
73015	Indigotine	Mg
29000	Chlorantine Fast Yellow 4GLL	Ni+Mg
74180	Solophenyl Turquoise Blue GL supra	Mg
63010	Alizarin Saphirole B	Mg+Ni
61570	Alizarin Cyanine Green CG	Mg+Ni
61570	Calcocid Alizarin Green CG	Mg+Ni
	Azocarmine B	Mg+Ni
	Azocarmine G	Mg+Ni
	Chlorantine Fast Rubine RNLL	Zn+Ni
35780	Chlorantine Fast Red 5BRL	Ni+Mg
45305	Basolan Chrome Brilliant Red 3BM	Ni+Zn
42080	Patent Blue A	Mg+Ni
50420	Nigrosin	Ni
42650	Pontacyl Violet C4BN	Ni+Mg
68205	Alizarin Rubinol 3G	Mg
	Pontamine Sky Blue 3BX	Ni+Mg
45190	Pontacyl Fast Violet VR	Ni+Mg
42045	Patent Blue V	Ni+Mg
	Palatine Fast Claret RNT	Ni
16540	Azo Fuchsine GA ex. conc	Ni+Mg
61530	Erio Anthracene Brilliant Blue 3G	Mg+Ni
24890	Paper Yellow CB	Mg+Ni
25380	Diphenyl Blue Red B	Mg+Ni
42155	Neptune Green	Ni+Mg
10316	Paper Yellow L	Ni+Mg

The developing apparatus may employ a tank, sponge or conducting roller, the photoconductive sheet being connected as the cathode. No special electrolytic conditions, e.g. voltage, etc. are required. Alternating current also may be used for development.

By using panchromatically sensitized photoconductive copysheets, full color prints or transparencies can be obtained. Three separate exposure and development steps are used to provide the cyan, magenta and yellow images, together providing a full range of color. The following procedures will illustrate useful techniques.

An electrolytically developable photoconductive zinc oxide copysheet was exposed successively to each of three color separation negatives, using contact techniques and a 200 watt projection bulb as light source. The copysheet was electrolytically developed after each exposure, by passing an anodically connected sponge roller over the exposed copysheet surface. The aqueous developer solution carried by the sponge roller contained 1% by weight of the acid dye, 3% magnesium acetate, and 0.5% $Nicl_2 \cdot 6H_2O$. The dyes used in the three development steps were Du Pont Paper Yellof (C.I. 10316), Pontacyl Fast Violet VR (C.I. 45190), and Pontamine Sky Blue 6BX (C.I. 24410), respectively. After each exposure and development step, the print was rinsed and dried at about 90° C., thereby removing excess developer and effectively "erasing" the differential photoconductivity pattern on the copysheet before the next exposure. A good full color print was obtained. Satisfactory full color prints can also be prepared from Kodacolor 35 mm. negatives by using a projection system and red, green, and blue filters for the cyan, magenta and yellow development steps respectively.

Images electrolytically produced on photoconductive copysheets in the manner described above can be transferred to separate receptor sheets by diffusion. Transparencies can be prepared by using as a receptor sheet a cellulose acetate backing having a gelatin coating which has been wetted with a dilute acid solution, e.g. a 5 percent acetic acid solution. When the wetted receptor sheet is pressed into contact with the image photoconductive sheet the colored dyes diffuse into the gelatin coating, providing a good quality transparency, usually in about 15 seconds. If the photoconductive copysheet contains a multicolor print thereon, the diffusion techniques can be used to prepare a multicolor transparency. Multiple copies on such receptor sheets can be prepared, the number of copies being limited only by the depletion of dye on the photoconductive copysheet. Separation negatives can be made from positive color transparencies using filters.

Various other embodiments of the present invention will be apparent to those skilled in the art without departing from the scope thereof.

I claim:

1. An electrolytic development process for developing an exposed copysheet having a photoconductive layer on a contiguous electrically conductive backing which comprises contacting the exposed surface of said copysheet with an electrolytically conductive developer solution having dissolved therein an ionizable anionic dye providing a negatively charged chromophore and a polyvalent metal cation selected from the group consisting of nickel, magnesium, zinc and calcium, and electrolyzing said developer solution, the electrically conductive backing of said copysheet being connected to serve as the cathode.

2. An electrolytic development process for developing an exposed copysheet having a photoconductive layer on a contiguous electrically conductive backing which comprises

(a) contacting the exposed surface of said copysheet with an electrolytically conductive aqueous developer solution having dissolved therein an acid dye providing a negatively charged chromophore and a salt of a polyvalent metal selected from the group consisting of nickel, magnesium, zinc and calcium, and

(b) electrolyzing said developer solution with the electrically conductive backing of said copysheet being connected to serve as the cathode.

3. The process of claim 2 wherein said polyvalent metal is nickel.

4. The process of claim 2 wherein said polyvalent metal is magnesium.

5. The process of claim 2 wherein said polyvalent metal is zinc.

6. The process of claim 2 wherein said polyvalent metal is calcium.

7. An electrolytic development process for developing an exposed copysheet having a photoconductive layer on a contiguous electrically conductive backing which comprises

(a) contacting the exposed surface of said copysheet with an electrolytically conductive aqueous developer solution having dissolved therein an acid dye providing a negatively charged chromophore and a salt of a polyvalent metal selected from the group consisting of nickel, magnesium, zinc and calcium,

(b) electrolyzing said developer solution with the electrically conductive backing of said copysheet being connected to serve as the cathode to develop a visible colored image thereon, and

(c) transferring said visible colored image thereon by diffusion means to an adjacent receptor sheet.

8. The process of claim 7 in which said receptor sheet contains a gelatin coating.

9. The process of claim 7 in which said receptor sheet contains a gelatin coating having a weak acid aqueous solution thereon.

10. An electrolytic development process for developing an exposed copysheet having a photoconductive layer on a contiguous electrically conductive backing which comprises:

(a) contacting the exposed surface of said copysheet with an electrolytically conductive aqueous developer solution having dissolved therein an acid dye providing a negatively charged chromophore and a salt of a polyvalent metal selected from the group consisting of nickel, magnesium, zinc and calcium, and

(b) electrolyzing said developer solution with the electrically conductive backing of said copysheet being connected to serve as the cathode to develop a visible colored image thereon,

(c) placing a receptor sheet in contact with said visible colored image and

(d) transferring said dye image to said receptor sheet by diffusion means.

11. The process of claim 10 in which said receptor sheet is transparent and the resulting product is a transparency.

12. The product obtained by the process of claim 2.

13. The product obtained by the process of claim 7.

14. In the electrolytic development process for developing an exposed photoconductive copysheet the improvement which comprises contacting the exposed surface of said copysheet with an electrolytically conductive developer solution having dissolved therein an acid dye providing a negatively charged chromophore and a polyvalent metal cation selected from the group consisting of nickel, magnesium, zinc and calcium, and electrolyzing said developer solution with said copysheet connected as the cathode.

15. An electrolytic process for preparing a full color reproduction which comprises

(a) exposing a panchromatically sensitized photoconductive copysheet to a light image,

(b) contacting the exposed copysheet surface with an electrolytically conductive developer solution having dissolved therein an ionizable yellow acid type dye providing a negatively charged chromophore and a polyvalent metal cation selected from the group consisting of nickel, magnesium, zinc and calcium,

(c) electrolyzing said developer solution, the copysheet being connected as the cathode, thereby developing a yellow image thereon, and

(d) repeating the aforementioned steps with a magenta acid type dye and cyan acid type dye respectively to obtain a full color print on said copysheet.

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