ELECTROPHOTOGRAPHIC IMAGING AND COPYING PROCESS

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Filed July 21, 1966. Ser. No. 566,845

Claims priority, application Japan, July 21, 1965, 40/43,837

Int. Cl. B44c 1/04

10 Claims

ABSTRACT OF THE DISCLOSURE

A recording method involving electrolytic deposition of material on a photoconductive element including providing a low adhesion layer on the surface of a photoconductive element, electrolytically depositing the material on the low adhesion layer of the photoconductive element, after exposure, and then transferring the deposited material from the low adhesion surface to the surface of a record receiving element.

This invention is concerned with an improvement in electrolytic development applicable to photography, reproduction, printing facsimiles, etc. and other such processes utilizing electrolysis.

For convenience of illustration there will now be described a method for the reproduction of images by subjecting a photoconductive layer to electrolysis while the photoconductive after-effect remains, after exposure to light or at exposure to light, thereby selectively depositing a material on the exposed portion in accordance with the extent of exposure. In practicing such method, a uniform mixture of a photoconductive zinc oxide and insulating resin is applied to a base plate having a high electric conductivity. After dark adaptation, the coated plate is subjected to image exposure, usually negative image exposure, and the plate is immediately subjected to electrolysis in an aqueous solution containing a dye forming ionic material, such as quaternary anhydro base, nickel chloride or silver nitrate, while using the zinc oxide layer as a cathode. Since the conductivity on the exposed portion remains, even after the cut-off of light, a large quantity of electric current is passed through the exposed portion, during the electrolysis, to form silver or nickel. The dye also deposits with the passage of electric current. (Cf. Japanese patent publications No. 6669/1955 and No. 11544/1964.)

When it is subjected to exposure and development three times by using a color negative as an original and filters of three primary colors in combination, a color positive can be obtained.

Moreover, it is possible to provide an original for offset printing by utilizing the change of pH at electrodes upon electrolysis, for example, to deposit a colorless metal hydroxide.

The method as described above can always be affected only if a photoconductive layer is used having a photoconductive after-effect, but it will be understood that various difficulties may be encountered in the practice thereon of a commercial basis.

Above all, the important problems are as follows:

(1) A paper or plastic film having a thin metal layer provided by vapor deposition or lamination, used as a base plate or support, is hard to handle as compared with usual papers, since the metal layer tends to be injured. The manufacture of such materials is costly. In obtaining a reproduction in color photography, in particular, the wet treatment should be carried out three times and thereafter, a support having a small degree of expansion and contraction in response to changes in temperature and humidity, such as polyethylene terephthalate, should be employed, since the expansion and contraction during the treatment are not favorable. This increases the cost for a support and limits its wide use as a printing material. A metal plate may be employed as a support, of course, but it is limited to a peculiar use.

(2) Aluminum has been found to be suitable for use as a thin metal layer in such elements, but in any case the surface condition on which a light sensitive layer is to be provided has a remarkable influence upon the finished image. That is, if the surface of a metal layer is coarse, a similarly coarse pattern appears in the image formed by electrolysis. Therefore, the finishing of the surface should be carried out with great care, which further increases the importance of the first above described disadvantage.

(3) Unless the coating of a photoconductive layer is carried out with great care, a number of pinholes are formed in the coating structure and a reduced metal deposits on these portions, which results in shortcircuits and retards image formation on other portions. An increase in the amount of the binder (insulating resin) is effective to make the photoconductive layer mechanically strong, but on the other hand, hinders the contact of the photoconductive material itself and tends to lower light sensitivity to a great extent.

(4) In color reproduction, it is desirable that the light sensitive layer have a light sensitivity over the whole range of wave lengths of visible rays. If so, the appearance of the light sensitive layer is naturally gray to black or at least is not purely white. Although any spectral characteristic is permitted, if three resolving negatives are specially provided, such complicated procedure is now out of the question. If the back-ground is of pure white, it is done at the sacrifice of the light sensitivity to maintain the appearance nearly white. For example, using zinc oxide as a photoconductive material, two or three sensitizing dyes are added so as to impart the panchromatic property thereto, since the intrinsic absorption range of zinc oxide is in the near ultraviolet portion. In this case, the amount of the dyes is maintained as low as possible because of the reasons mentioned above. Thus, possible increase of light sensitivity is hereby given up and the utilization of colored photoconductive material is similarly restricted.

(5) A photoconductive layer containing zinc oxide, being chemically active and having photocatalytic action under radiation of light, tends to decompose organic compounds. Therefore, images formed thereon by electrolysis discolor in the course of long storage, and this is accelerated by zinc oxide.

We have made efforts in order to solve a number of problems as described above and succeeded thereby in the following novel method:

A photoconductive layer is so composed that at least its surface is of low adhesiveness and an electrolytic product formed by electrolysis can be readily stripped from the photoconductive layer, so that the image consisting of the electrolytic product is transferred to a record receiving element. This transfer should be substantially complete to such an extent that the photoconductive layer can be reused after the transfer. If this is done, the light sensitive material can be used repeatedly. The cost per one print can be overlooked, even if the cost required for the production of the light sensitive material is high. The foregoing problems (1) and (2) can be solved by a single effort. It will be understood that problems (4) and (5) are also solved. Moreover, it is found that the remaining problem (3) is somewhat improved by the presence of the surface layer of our invention.
In a color reproduction, if an image is transferred to a suitable surface, after exposure and development three times, the cost required for a material of the finished print is reduced remarkably, because it does not matter whether that surface is of a material which is expansible and contractible. In addition, the light sensitive layer, after the transfer, is returned to a state suitable for reuse.

The structure of the light sensitive material of our invention is shown in the accompanying drawing, wherein 1 is a support, such as paper, plastic film and a metal plate, 2 is an electrically conducting layer such as an aluminum vapor deposition layer or high conductive metal film, a subbing layer is provided between 1 and 2 for the purpose of strengthening the adhesion thereof. As occasion demands, 3 is a photoconductive insulating layer, for example consisting of a uniform mixture of zinc oxide and a binder and 4 is a thin low-adhesion layer, the surface of which, for example, consists of a silicone-type surface releasing agent. In this layer, if necessary, may be incorporated a material miscible with a silicone type surface releasing agent, such as, nitro-cellulose, polyvinyl acetate, carboxymethyl cellulose, and polyvinyl alcohol.

Silicone oils and waxes may be used for the low adhesive layer in accordance with the use. The surface layer is not present as a clear, independent layer, but may be uniformly mingled with a photoconductive layer so as to give a low adhesion surface. Of course, the whole body of a light sensitive material may be so composed. The important point lies in that the surface has a low adhesiveness.

The low adhesion surface means a surface having a low affinity to a number of strongly viscous and adhesive materials, even if pressed strongly against each other, and a good stripping property therefrom. It has been well known that paraflin-type compounds exhibit low adhesive-ness. Therefore, polyethylene has such property. Fluorine resins have the same property. A layer consisting of a silicone type surface releasing agent that has been marketed of late exhibits more excellent properties than those described above or has no affinity to very viscous and adhesive materials. The characteristic of the low adhesion layer is represented by the force required to strip a strongly viscous and adhesive material, to be the standard, from the layer onto which the adhesive material is pressed in a predetermined manner. In the present invention, the force required for stripping a strongly adhesive layer is set at a rate of about 30 cm./min. onto the low adhesion layer is preferably 100 g./cm. or less. Of course, the lower the required force the better is the low adhesion layer.

Silicone type surface releasing agents are on the market in forms of aqueous emulsions and organic solvent solutions and it is found that any of them may be employed in our invention. In particular, the use of the former raises no fear of attacking the photoconductive layer, because the photoconductive layer often uses a binder miscible with organic solvents and immiscible with water. However, there may be disadvantage in that the coated surface is not uniformly wetted. In the case of using an organic solvent solution, on the other hand, a uniform thin layer is readily formed but the binder in a photoconductive layer is often dissolved therein. In such cases a special coating procedure should be devised.

The thickness of the surface layer, if it covers the whole surface, should be as thin as possible. A thin layer hinders the passage of electric current, resulting in reduction of the practical sensitivity and operating speed in our invention. It has been made clear by our experiments that the electrolysis takes place without trouble at a thickness up to several microns, a preferred range being 1 micron or less than 2 microns.

In the present invention, furthermore, the decrease of pinholes is observed as an unexpected merit. This merit will enhance the great improvement of our invention, because we aim to use a photoconductive layer as many times as possible. The invention will be further illustrated by the following examples.

Example 1

100 parts of photoconductive zinc oxide, 25 parts of a copolymer of styrene and butadiene “Pioliic S-7” (manufactured by Goodyear Tire & Rubber Co.) and 75 parts of toluene were charged to a ball mill of porcelain and mixed for a long time to give a uniform dispersion. The dispersion was applied by spraying to a smoothly polished cylinder of aluminum to a thickness of 25 to 28 microns after drying. After evaporating the solvent, the photoconductive layer was rubbed with a cotton piece immersed in the following treating solution:

<table>
<thead>
<tr>
<th>Parts</th>
<th>3.476,659</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone surface releasing agent in aqueous emulsion</td>
<td>30%</td>
</tr>
<tr>
<td>Curing catalyst solution for the foregoing emulsion</td>
<td>2.3</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>0.4</td>
</tr>
<tr>
<td>Water</td>
<td>80.6</td>
</tr>
</tbody>
</table>

The thus treated cylinder was allowed to stand in a furnace at 150° C. for 20 minutes to cure the surface layer thereby.

This light sensitive material, after standing in a dark place for 2 hours, was exposed through a negative image and immediately developed by the following electrolytic developing solution:

<table>
<thead>
<tr>
<th>Parts</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver nitrate</td>
<td>1.35</td>
</tr>
<tr>
<td>Thiourea</td>
<td>4</td>
</tr>
<tr>
<td>Acetamide</td>
<td>4</td>
</tr>
<tr>
<td>Water</td>
<td>to 100 parts</td>
</tr>
</tbody>
</table>

In the electrolysis, the zinc oxide layer was used as cathode and a direct current of 4 v. was applied. A silver image was obtained as a positive image. After drying, the image was transferred completely to a marketed cellulose base tape by pressing it lightly to the surface of the photoconductive layer. Thirty different images could be obtained from the same photoconductive layer by repeating the similar steps while bringing the light sensitive material into a dark adaptation state. There was little difference in the image quality of the first image and thirtieth image, and the light sensitive layer could be used more.

It is evident from the foregoing experiments that the surface layer has no influence upon the passage of electrolytic current in spite of the fact that it is of an insulating material. The adhesion of the low adhesion layer and photoconductive layer is good enough to resist to repeated uses. The generation of pinholes was not observed before the tenth treatment. The good adhesion of the low adhesive layer and the photoconductive layer is likely due to the fact that there is no effective force between the photoconductive layer and the low adhesive layer, since an adhesive tape has no affinity to the low adhesion layer. It is natural that the formation of pinholes can be suppressed by performing the stripping of an adhesive tape with great care.

When a portion free of a low adhesive layer is subjected to the similar tape treatment for comparison, a part of the image and photoconductive layer was transferred to the side of the tape and it could not be reused. Furthermore, another method comprising using a thermoplastic film in place of the adhesive tape and transferring an image with heating, after placing it upon the image, was favorably carried out. In general, a thermoplastic film is superior to an adhesive tape, since the adhesive layer of the latter contains often a plasticizer or solvent for dyes, whereby an image is blurred in the course of a long storage.

Example 2

The following dyes were added to the mixture of Example 1 for dye-sensitization to impart a light sensitivity
over the whole visible range and applied to the same support as in Example 1, followed by drying.

![Chemical structure diagram]

To the thus formed light sensitive layer was applied, by spraying, a silicone surface releasing agent having the following composition:

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Shin-Etsu Silicone KS-705 (non-volatile matters 30%)</td>
<td>16.7</td>
</tr>
<tr>
<td>Catalyst for the foregoing</td>
<td>0.6</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>0.05</td>
</tr>
<tr>
<td>Toluene</td>
<td>82</td>
</tr>
</tbody>
</table>

The coating was then heated at 150°C to cure completely. The light sensitive layer was brought into a dark adaptation state and subjected to exposure three times by the use of a color negative as an original and a red, blue and green filter. After exposure through the red filter, it was subjected to electrolytic development using a cyan dye. Similarly, a yellow dye was used for the blue filter exposure and a magenta dye for the green filter exposure. As the cyan dye, Alcan-Blue-5GN was used. Yellow thionium compound obtained by reacting bis(chloromethyl)-4,4'-bis(6-methylbenzimidazol-2-)-azobenzene and N,N,N', N'-tetramethylthiourea as the magenta dye. The methods for the synthesis of these dyes are described in Japanese patent publication No. 15,444/1965.

When the image obtained on the light sensitive layer was rubbed with fingers, it was easily taken off. After drying the light sensitive layer, a Baryta paper coated with gelatin was moistened a little with water and pressed thereto, whereby the color image was transferred substantially completely. The light residual image could be readily removed by applying a strong stream of water thereto and the light sensitive layer was thereby returned to a state ready for reuse.

It will be understood from the above description that a novel photographic process having the following advantages is made possible in accordance with the invention:

(1) Any support can be adapted therefor.
(2) Any light sensitive layer can be used, because its color tone and mechanical properties have no influence upon the final prints.

(3) Restrictions in respect of a cost for a light sensitive material can be relaxed to a great extent, because the light sensitive layer is resistant to repeated uses.

(4) Formation of pinholes in the light sensitive layer during electrolysis is decreased.

(5) The contrast and the density of an image transferred can be controlled. For example, when a sufficient density of an image is not obtained by one electrolytic development, the image is once transferred, and the same image is put on after the second exposure and development. The control of contrasts will be performed similarly.

The present invention is applicable to other recording methods accompanied by electrolysis. One of them, for example, comprises providing a material consisting of an electrically conductive thin layer covered with an insulating coating, breaking the insulating coating by means of a pen pressure or discharge in accordance with an image, subjecting this, as a master, to electrolysis in a suitable electrolytic bath, whereby to deposit a metal, dye or metal hydroxide on the conductive portions from the electrolytic bath, and transferring the thus deposited material to a transfer material by suitable means. A number of reproductions are thereby obtained, but it is very important in this method also that the transfer be satisfactorily carried out. In order to apply the present invention to such case, the following procedure is preferred. A master obtained once by suitable means is coated thinly and uniformly with a silicone oil, fluorinated hydrocarbon oil or silicone surface releasing agent. The resulting layer acts as a surface releasing agent without hindering the passage of electric current, resulting in a similarly remarkable improvement.

Example 3

As the surface releasing agent of Example 2 required much time for curing, a solution of polymethylsiloxane having a viscosity of 100 cp. at normal temperature in toluene was applied to an original plate by spraying in place of the surface releasing agent of Example 2. This method appeared to be similarly effective for our aims.

An electrically conductive pattern than can be adapted for electrolytic development may be obtained by many other methods. For example, in using a light sensitive layer whose electric resistance is remarkably lowered by applying pressure thereto or a recording material comprising an electrically conductive thin layer continuously provided with such a pressure sensitive layer, that is, to be transferred to some other support by pressure, a master will be readily obtained by a pen pressure.

When the present invention is applied to those methods in combination, images obtained by electrolysis are readily transferred to other transfer materials to thereby give a plurality of prints.

A permanent electrically conductive pattern may be obtained by providing a photoconductive layer utilizing a photoconductive material to be reduced electrolytically, for example, zinc oxide and/or indium oxide and subjecting the photoconductive layer to electrolysis in aqueous solution of alkali metal halide, whereby to reduce the compounds in the photoconductive layer.

A still further application of our invention consists in making "facsimiles." Our invention gives records not accompanied by discolorations or changes in color with the passage of time in a method wherein electric signals transmitted in accordance with information modulate the voltage of a needle-like electrode to color an electric current color forming paper. For example, when a low adhesion layer is applied thinly to the surface of a metal drum, an electrolytic color forming solution is flowed thereon and the recording is carried out by a needle-like electrode, dyes and other electrically conducting products are deposited on the low adhesion layer once. The drum is then immersed in water with revolving to wash electrically conductive salts and color forming components off, and
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subjected to transferring to a suitable support. The drum can be reused, if necessary, by washing with water again.

The present invention, as is evident from the above descriptions, will be applied to all technical fields utilizing electrolysis, such as electrolytic electrophotography, printing, printed circuits and facsimile.

What is claimed is:

1. A recording method involving electrolytic deposition of material on a photoconductive element which comprises providing a low adhesion layer on the surface of said photoconductive element, electrolytically depositing a material on the low adhesion layer of the photoconductive element, after exposure, and then transferring the deposited material from the low adhesion surface to the surface of a record receiving element.

2. The method of claim 1 further comprising restoring the photoconductive element to a condition ready for reuse.

3. The recording method according to claim 1 wherein said low adhesion layer comprises a silicone surface releasing agent.

4. The recording method according to claim 1 wherein said electrolytic deposition is conducted in an electrolyte containing a silver salt and a silver image is formed on the low adhesion layer and is then transferred to the surface of the record receiving element.

5. The recording method according to claim 1 wherein the photoconductive layer of said photoconductive element contains at least one dye subjected to dye sensitization and said electrolytic deposition is conducted in an electrolyte containing at least one dye to deposit a color image on the low adhesion layer.

6. A recording element for electrolytic recording comprising an electroconductive layer, operative as an electrode during the electrolysis and a photoconductive layer, coated on said electroconductive layer said photoconductive layer having a low adhesion surface.

7. The recording element according to claim 6 wherein said low adhesion surface comprises a silicon surface releasing agent.

8. The recording element according to claim 6 wherein said electroconductive support is aluminum and said photoconductive layer comprises zinc oxide.

9. The recording element according to claim 8 wherein said support is selected from the group consisting of paper and plastic film, said electroconductive layer is aluminum, said photoconductive layer comprises zinc oxide and said low adhesion layer comprises a silicone surface releasing agent.

10. A recording element for electrolytic recording comprising a support, an electroconductive layer, operative as an electrode during the electrolysis, on said support, a photoconductive layer on said electroconductive layer and a low adhesion layer on said photoconductive layer.

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