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3,511,650

ELECTROPHOTOGRAPHIC IMAGING PROCESS

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14 Claims

ABSTRACT OF THE DISCLOSURE

Process of image formation whereby a photoconductive copy sheet capable of electrolytic development is exposed to activating radiation. A vaporizable material is then brought in the vicinity of the photoconductive surface and is electrically modified by oxidation, reduction, masking or complex formation in the more conductive areas. A receptive surface capable of changing color upon contact with the vaporizable material is positioned adjacent to the photoconductive copy sheet and said vaporizable material is transferred upon heating copy sheet.

This application is a division of application Ser. No. 181,796, filed Mar. 22, 1962, now U.S. Pat. No. 3,363,556.

This invention relates to an integrated process for the reproduction of a light image and to materials employed therein. In one aspect, this invention is directed to a process for the production of multiple prints from a light image. In still another aspect, this invention relates to a process for preparing a master copysheet of a light image which can be used to provide multiple copies thereof.

A recently developed image reproduction process involves electrolytically developing permanent and visible images on suitable, strongly photoconductive copysheets after exposure to light images. This process, described more fully in U.S. Pat. No. 3,010,883, includes the electrolysis of an electrolytic developer and particularly the selective electrodeposition of a metallic or other visibly distinct coating at the exposed portions of the photosensitive surface, e.g. by electrolytic reduction. Strongly photoconductive copysheets suitable for use in the above method are described in U.S. Pat. No. 3,010,884. To improve the sensitivity of such photoconductive copysheets, various optical sensitizers have been suggested. However, many of the dye sensitizers tend to discolor the surface of the photoconductive copysheet and detract from the quality of the image produced thereon. In addition, it has been desired to provide a simple, efficient means for making multiple copies from the electrolytically developed copy-sheet.

It is therefore an object of this invention to provide a simple, economical method for making multiple copies of a radiant image.

It is another object of this invention to provide a method for utilizing an electrolytically developed, strongly photoconductive copysheet as a master for the thermal preparation of a heat stable copy thereof.

Still another object of this invention is to provide a reproduction process involving a photoconductive copy-sheet in which the visible appearance of the photoconductive copysheet, both prior and subsequent to electrolytic development, does not substantially affect the copies produced therefrom.

Yet another object of this invention is to provide a process for preparing multiple copies of a light image.

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Still another object is to provide a process for the preparation of multiple copies of a radiant image from a reusable photoconductive copysheet.

As used herein, "thermal processes" refers generally to processes requiring the use of heat.

The process of this invention comprises exposing a photoconductive, electrolytically developable copysheet to produce a differential conductivity pattern thereon, electrolytically forming a pattern of a vaporizable image forming material on the exposed surface corresponding to said differential conductivity pattern, positioning said surface of the copysheet adjacent a receptor surface, and heating said copysheet to affect the selective vapor transfer of said vaporizable image forming material to said receptor surface and the formation on said receptor surface of a visible image corresponding to said differential conductivity pattern. In one embodiment the image forming material is transferred as a vapor to a receptor (usually in sheet form) containing a color-forming coreactant, the vaporized image forming material and the color-forming coreactant interacting on said receptor to form visibly distinct image areas. In another embodiment, where the vaporized image forming material is itself strongly colored, no further reactant is required on the receptor, and the receptor sheet color provides a visible contrast with the image forming material condensed thereon.

Strongly photoconductive copysheets suitable for the practice of this invention include those described in U.S. Pat. No. 3,010,884 and generally comprise a strongly photoconductive layer containing such materials as photoconductive zinc oxide, photoconductive indium oxide, etc., superimposed on a contiguous, electrically conductive backing or support, such as aluminum foil. Optical sensitizers, e.g. Acridine orange, may be incorporated into the photoconductive layer to improve the spectral response. Since the color of the copysheet does not necessarily affect the quality of the thermally prepared copies, the amount of sensitizer in the photoconductive layer can be varied widely to achieve optimum results. The photoconductive layer may be overcoated with a water permeable layer, such as a film forming silica. Film forming silicas are generally capable of forming a stable aqueous colloidal sol with a particle size in the 1 to 100 millimicron diameter range, preferably from about 10 to about 50 millimicrons, and their preparation may be effected by procedure described in U.S. Pat. No. 2,244,325. Further description of such electrolytically developable photoconductive copysheets having glossy, water permeable, cohesive and relatively transparent silica films superimposed on the photoconductive layer is given in U.S. Ser. No. 140,932, filed Sept. 2, 1961, now Pat. No. 3,165,458.

After exposure of the photoconductive copysheets to a source of activating irradiation, e.g. actinic irradiation such as visible light, X-rays, electron or proton beam, etc., a differential electrical conductivity pattern is created in the photoconductive layer, corresponding to the information carried by the activating irradiation, and is utilized for selectively creating on the conductive areas by electrolytic means a pattern of vaporizable image forming material. Exposure of and electrolytic deposition on such strongly photoconductive copysheets is described in U.S. Pat. No. 3,010,883, as mentioned earlier.

For purposes of this invention, "vaporizable image forming material" is defined as a material readily vaporized at temperatures above room temperature and below 300° C., preferably between about 60° C. and about 250° C., and which is capable of affecting a color change either by chemical reaction with other chemical compounds or, when itself strongly colored, by condensation from the vapor onto a surface without chemical reaction. Whether the vaporizable image forming material is of the reactive or non-reactive type, therefore, it should be essentially

non-vaporizing at normal room and storage conditions and can be described as normally solid under such conditions.

A variety of techniques may be used to convert the differential conductivity pattern of the exposed copysheet into a differential pattern of vaporizable image forming material. However, in every instance, the conversion is accomplished electrolytically or electrophoretically. For purposes of this invention, both "electrolytic" and "electrophoretic" will be generically described as "electrolytic," although electrophoresis involves the use of charged particles other than charged ions. In practice, the vaporizable image forming material may be selectively deposited on the copysheet surface by electrolysis (with or without further modification thereon) or a thin film of vaporizable image forming material may be uniformly provided on the copysheet surface and electrolytically modified in selected areas to alter its vaporizability and/or its image forming properties. The former will be referred to as "electrolytic deposition," and the latter will be referred to as "electrolytic modification," it being understood, however, that both techniques may be employed simultaneously.

Electrolytic deposition is accomplished by depositing the normally stable vaporizable image former directly from solution or suspension. When the electrolytic bath contains the vaporizable image former or its electrolytic precursor in solution, the copysheet is connected either as anode or cathode, depending on the electrical charge on the ions. When the electrolytic bath contains the vaporizable image former or its electrolytic precursor in suspension, a suitable charge bearing carrier, e.g. colloidal alumina, is preferably used to effect migration toward the copysheet surface, where it is deposited. In such a deposition process, the vaporizable image forming deposit may consist of an interreactive volatilizable image forming compound which, upon vapor transfer from the copysheet to the receptor, reacts with a coreactant thereon to form a visible image. Such interreactive volatilizable image forming compounds include, for example, oxidizing and reducing agents, the corresponding coreactant being a compound which alters its color value upon oxidation or reduction respectively. One preferred class of interreactive volatilizable image forming compounds are prepared from the quaternary ring bases. Illustrative of the useful quaternary ring bases are 1-ethyl quinolinium iodide, 1-ethyl quinaldinium iodide, 1-ethyl pyridinium bromide, 1-ethyl-2,6-dimethyl quinolinium iodide, 1-butyl pyridinium bromide, 1-ethyl-2-methyl pyridinium bromide, 1-ethyl-4-methyl pyridinium bromide, etc., which electrolytically deposited the corresponding organic reducing agent at the cathode from aqueous medium. Other suitable materials which electrolytically deposit a volatilizable reducing agent include quinone, aromatic nitro compounds capable of reduction to amines, aromatic hydroxyl amines, etc. Volatilizable oxidizing agents, e.g. the oxidation product of hydroquinone, catechol, tetrachlorohydroquinone, tetrabromohydroquinone, aminophenol or oxidizing agents such as N-chlorosulfonamides, etc. can also be electrolytically deposited when the copysheet is connected as anode, usually from an electrolyte containing appropriate charged particles.

Reducible coreactants, such as silver behenate, etc. contained uniformly on the receptor sheet may be reduced by a vaporized reducing agent, producing a color change on the receptor. The reducible coreactants on the receptor sheet, on the other hand, may be themselves intensely colored and capable of losing or changing color intensity or value upon contact with a vaporized organic reducing agent, as illustrated by reducible dyes, such as methylene blue, crystal violet, and Malachite green. If the receptor sheet contains a relatively colorless compound which forms a colored complex, the vaporizable image forming deposits may contain the corresponding complexing

agent, e.g. catechol (forms a complex with iron compounds), thereby forming the colored complex on the receptor sheet upon vapor transfer.

As mentioned earlier, when the vaporizable image forming material is itself intensely colored, it may be transferred directly in vapor form to the receptor surface, where its condensation forms a visible pattern corresponding to the original image without further chemical reaction. No coreactant is thus required on the receptor sheet. Both water soluble and water insoluble dyestuffs may be deposited, the latter being deposited from a colloidal suspension, preferably from a suspension of positively charged particles.

Electrolytic modification may also be used to provide a selective imagewise coating of vaporizable image forming material on the copysheet surface. Instead of electrolytically depositing the vaporizable image former, the copysheet may be coated uniformly with a thin film of a material which is then modified by the electrolytic reaction to alter its vaporizability and/or its image forming properties. This modification may be accomplished by selective electrolytic destruction, electrolytic masking or electrolytic immobilization of the vaporizable image forming material on the more conductive areas of the copysheet surface, as is hereinafter described.

The mechanism of electrolytic destruction of a vaporizable image former can be accomplished by electrolytic oxidation of a vaporizable reducing agent uniformly coated on or included in the copysheet surface. Such reducing agents including pyrogallol, catechol, methyl gallate, aminonaphthols, 4-methoxy naphthol, etc., which are anodically oxidized on the more conductive areas of the copysheet surface. Reducible coreactants, e.g. silver behenate, etc. contained on the receptor sheet are then reduced when contacted with the vaporized, unoxidized reducing agent, thereby producing a visible color change on the receptor surface and a visible reproduction of the original image. These vaporizable reducing agents may also be electrolyzed cathodically in a medium that provides a relatively high pH in the light struck areas, e.g. an aqueous bath containing soluble magnesium salts. When exposed to air in such a high pH environment, the vaporizable reducing agents (e.g. 4-methoxy naphthol) are readily oxidized in the more conductive areas, thus leaving the unoxidized reducing agent only in the background areas for vapor transfer to the receptor sheet and interreaction with silver behenate or other suitable material which changes color value upon reduction.

The mechanism of electrolytic masking involves a photoconductive copysheet containing on or immediately under its surface a uniform layer of a vaporizable image former and the selective electrolytic deposition of a mask or coating to cover or fix such image forming compound in the more conductive areas. The mask is usually a higher molecular weight, e.g. polymeric, material which is desirably deposited from latex and which provides a relatively impermeable barrier to vapor. Either cathodic or anodic deposition may be used, depending on the charge on the latex particles. Illustrative of suitable masking materials of an insulative nature are the organic chelates or coordination compounds and amine derivatives, such as amine salts or quaternaries, including the Werner type chromium complexes of fatty acids (e.g. Quillon chrome complex, a product of E.I. du Pont de Nemours and Co., Wilmington, Del.), various fatty amine derivatives (e.g. Armeens and Arquads, Armour Industrial Chemical Co., Chicago, Ill.), amine containing resins (e.g. Versamid resins, General Mills, Inc., Minneapolis, Minn.), condensation products of polymerized unsaturated fatty acids (e.g. dilinoleic acid) with aliphatic amines (e.g. ethylene diamine), polyethylene, polytetrafluoroethylene, polytrifluorochloroethylene, synthetic rubbers, polyvinyl acetate, polystyrene, butadiene-styrene copolymers, butadiene-acrylic acid copolymers, natural

rubber, polyvinylidene chloride, etc. After the deposit of sufficient masking material to inhibit the vapor transfer of the image forming material in the image areas, the unmasked image former in the background areas is more readily transferred in vapor form to the receptor sheet.

Electrolytic immobilization also provides a method for creating an imagewise coating of vaporizable image forming reactant on the copysheet surface. In contrast to techniques which alter the image forming properties of the vaporizable material, this method generally involves a change in vaporizability of the image former. The copysheet surface may be coated with a vaporizable image former which forms a complex or chelate of lower vaporizability, e.g. chelating or complexing of a phenolic reducing agent, coated uniformly over the copysheet surface, by cathodic electrolysis of a metal ion that complexes with the phenolic reducing agent. As one specific example, if a copysheet is uniformly coated with catechol and exposed to a light image, cathodic electrolysis with an electrolytic bath containing ferrous or ferric ion produces a colored complex in the more conductive (and more alkaline) areas of the copysheet surface. This complex has significantly lower vaporizability than the catechol. Hence, upon the uniform application of heat to the copysheet, only the free catechol in the background areas is vapor transferred to the receptor sheet, where the catechol reduces a material, such as silver behenate, or forms a complex with another material thereon to produce a visible image.

In the electrolytic modification techniques, the vaporizable image forming material may be coated uniformly in a thin film over the photoconductive surface of the copysheet after exposure to the light image and before electrolysis. When the film of vaporizable image forming material is relatively transparent to the activating irradiation incident to exposure and creation of a differential conductivity image pattern on the copysheet, it may of course be present over the photoconductive surface before exposure. It has been found that extremely small amounts of the vaporizable image forming material uniformly distributed over the copysheet surface are effective for the thermal preparation of multiple copies from the copysheet in this manner. As mentioned earlier, the vaporizable image forming material may also be included in a coating in or near the surface of the photoconductive copysheet.

As receptor surfaces, it is possible to use fabric, paper, plastic film, metal foil or plate, etc. Porous flexible sheets are sometimes desirable if an image forming coreactant is incorporated either in the receptor sheet or on the surface thereof. Transparent receptor sheets may be used to provide transparencies from which projected light images can be obtained. This is often important if an enlargement of the image is desired, as in the case of microfilm.

Both positive and negative prints can be obtained on the receptor sheets. For example, if the receptor sheet contains a colored coreactant which is rendered colorless by reaction with a reducing agent vaporized from the more conductive areas of the copysheet, a positive of the original radiant image may be obtained. Conversely, if the coreactant is reduced to a more intensely colored product, a negative print may be obtained. Methylene blue, Crystal Violet and Malachite green, when contained in the receptor sheet, are examples of coreactants which are converted to a colorless form upon reduction. Silver behenate and tetrazolium compounds exemplify coreactants which become more intensely colored upon contact with a vaporized reducing agent.

After the photoconductive copysheet has been exposed to the irradiant image, or simultaneous therewith, it is electrolytically developed to provide a differential deposit of vaporizable image forming material on the photoconductive surface using any of the electrolytic deposition or electrolytic modification techniques described earlier.

When such photoconductive copysheets are connected as anodes during electrolytic development, a rectification effect has been observed which tends to increase the overall resistance to current flow. By providing a relatively light transmissive, electrically conductive surface coating on the photoconductive layer (e.g. metal, etc.) as described in U.S. patent application Ser. No. 113,290, filed May 29, 1961 now Pat. No. 3,127,233, this rectification barrier may be markedly reduced, and anodic electrolytic development of the photoconductive copysheet is facilitated.

After electrolytic development, the copysheet is then placed in close proximity to, preferably in physical contact with, a receptor sheet. Heating the copysheet slightly above the vaporization point of the vaporizable image former, typically by passing both the copysheet and the superimposed receptor sheet through a heated mangle, ironing device or commercial thermographic copying machine with the heat being preferably applied to the backside of the photoconductive copysheet, vaporizes the image forming material and affects its vapor transfer into the adjacent receptor sheet. This vapor transfer step can be repeated with one or more receptor sheets to make multiple copies from the photoconductive copysheet master until the vapor supply is exhausted. The application of heat to the copysheet also tends to erase the differential conductivity pattern thereon, thus in some cases permitting reuse of the copysheet upon exhaustion of the vaporizable image former on its surface.

Apparatus suitable for heating the copysheet may conveniently consist of a line source of light including a tubular bulb having a linear filament and mounted within a focused reflective housing, as described in U.S. Pat. No. 2,740,895. Another suitable form of apparatus is described in U.S. Pat. No. 2,891,165. A heated platen may also be employed.

The following examples will illustrate the invention and are not intended to limit the scope thereof.

EXAMPLE I

This example illustrates the cathodic electrolytic deposition of an organic reducing agent.

A photoconductive copysheet containing a strongly photoconductive layer of zinc oxide and butadiene-styrene copolymer (30:70 mol ratio) is a pigment to binder ratio of about 4/1 as binder on an aluminum foil backing was exposed to a visible light image. The exposed copysheet was electrolytically developed, the aluminum backing being connected as cathode, by slowly passing a sponge developer roller (anode) over the surface with the application of a 40 volt D.C. electrical potential. The sponge developer roller contained a 5% aqueous solution of 1-ethyl pyridinium bromide. The thus developed copysheet was then placed against a paper receptor sheet containing silver behenate and heated between metal plates for approximately one second at 120° C. Hot rollers or any other means for uniformly heating the copysheet for a specific time interval may also be used. A brown-black negative image is developed on the receptor sheet. This operation can be repeated to obtain further copies in the same manner and permits the preparation of multiple enlarged prints from a microfilm transparency. The final prints on opaque receptor sheet material are directly readable if the original visible light image in a mirror image of the desired print.

EXAMPLE II

This example illustrates the preparation of a transparency using the cathodic electrolytic deposition of an organic reducing agent.

A transparent receptor sheet was made by coating a polyethylene terephthalate film with an alcoholic solution of triphenyl tetrazolium and butyral polyvinyl plastic. Following the procedure set forth in Example I, a negative transparency was produced on the receptor sheet after heat treatment at 100° C.

EXAMPLE III

This example illustrates the preparation of a positive transparency or opaque print using electrolytic deposition of an organic reducing agent.

A receptor sheet previously primed with colloidal silica was treated with a 3% solution of crystal violet in ethyl alcohol to form a blue colored receptor sheet. A photoconductive zinc oxide copysheet was then exposed to a visible light image and electrolytically developed with a 5% solution of 1-ethyl pyridinium iodide in the manner described in Example I. The exposed copysheet was then placed against the blue colored receptor sheet and heated briefly to 120° C. A positive white on blue copy was obtained, the crystal violet being reduced to leuco form in the areas corresponding to the visible light struck areas of the photoconductive copysheet.

EXAMPLE IV

This example illustrates the electrolytic deposition of a vaporizable dyestuff.

Two-hundred grams of water and 6 grams of colloidal alumina (AlOOH) were mixed in a blender for 5 minutes. Three grams of Du Pont Oil Yellow N, a water insoluble dye (Color Index 11020) was then added and dispersed by further blending for 10 minutes. A photoconductive zinc oxide copysheet of the type described in Example I was exposed to a visible light image and was electrolytically developed using the above dispersion, the copysheet being connected as cathode. After less than 5 seconds at a potential of 40 volts D.C. the colloidal alumina (the particles of which bear a positive charge) and dye deposited selectively on the light struck areas of the copysheet surface. The copysheet was then removed from the electrolytic bath, the dyed surface placed in contact with a paper receptor sheet, and heat was applied uniformly over the back of the copysheet (about 250° C.). After separating the sheets a yellow image corresponding to the original light image was formed on the receptor sheet.

EXAMPLE V

This example illustrates the electrolytic deposition of a vaporizable chelating agent.

Two-hundred grams of water and 6 grams of colloidal alumina (AlOOH) were blended for five minutes. Then three grams of dimethylglyoxime, a water insoluble complexing agent, was added and dispersed by further blending for 10 minutes. A photoconductive copysheet, as described in Example I, was exposed to a visible light image and was electrolytically developed using the above dispersion, the copysheet being connected as cathode. After less than 5 seconds at a potential of 40 volts D.C. the colloidal alumina and dimethylglyoxime had deposited on the light struck areas of the photoconductive surface. This copysheet was then removed from the electrolytic bath, and the photoconductive surface thereof was placed in contact with a receptor sheet containing a nickel soap. The back of the copysheet was heated briefly and uniformly to 250° C. Upon separating the sheets, the receptor sheet was observed to contain a red image formed from the nickel-dimethylglyoxime complex. Ten copies were prepared from this copysheet by repeating the heating sequence with further similar receptor sheets.

EXAMPLE VI

This example illustrates the electrolytic destruction technique in which an organic vaporizable reducing agent is selectively oxidized in a high pH environment.

A photoconductive copysheet having a coating of zinc oxide and butadiene-styrene copolymeric binder (4/1 wt. ratio) on an aluminum foil backing was coated with a thin film of 4-methoxy naphthol and buffed lightly to insure a thin continuous coating. The copysheet was dark adapted and exposed to a light image. With the aluminum foil connected as cathode, a porous plastic (Porelon) roller containing a 5% aqueous solution of cesium nitrate

was passed slowly over the surface. The anode was embedded in the roller. The potential applied was 40 volts D.C. After electrolytic development the increased alkalinity of the more conductive areas caused the 4-methoxy naphthol thereon to oxidize when exposed to air. The copysheet was then placed adjacent to a paper receptor sheet containing silver behenate and heated at 120° C. to form a visible blue-black positive image on the receptor sheet. The heating step was repeated to provide multiple copies.

Other suitable electrolytes are ionizable salts of barium, magnesium, calcium, potassium and sodium. Hydroquinone operated in similar fashion when used in place of 4-methoxy naphthol.

EXAMPLE VII

This example will illustrate electrolytic immobilization by means of chelate formation.

A dark adapted photoconductive copysheet, as in Example I, was coated with catechol and exposed to a light image and was cathodically electrolyzed in similar fashion. The porous roller contained a 5% aqueous solution of ferrous ammonium sulfate. The electrolyzing voltage was 20 volts D.C. The ferrous ion reacted with the catechol in the light struck areas, forming a colored complex having a lower vaporizability than catechol. When the electrolytically developed copysheet was placed adjacent a receptor sheet containing silver behenate and heated to 120° C., a positive visible image was produced on the receptor, the silver behenate being reduced by vaporized catechol.

In a similar fashion, a dithiooxamide can be electrolytically complexed with nickel, using an aqueous nickel salt electrolyte, and the uncomplexed dithiooxamide can be vapor transferred to a receptor sheet containing a complexible nickel salt, producing a positive print.

EXAMPLE VIII

This example illustrates electrolytic destruction by anodic electrolytic oxidation of a vaporizable reducing agent.

A photoconductive zinc oxide copysheet similar to that described in Example I was uniformly vapor coated on the zinc oxide surface with aluminum, the aluminum layer having a 30% transmissivity to visible light from a tungsten source. The vapor coated surface was then coated by buffing with 4-methoxy-1-naphthol, and the resulting sheet was exposed to a light image. With the electrically conductive substrate of the copysheet connected as anode, electrolytic development was effected for 3 seconds at 40 volts D.C., using a 5% aqueous solution of sodium acetate as the electrolytic bath. This resulted in the selective oxidation of the 4-methoxy-1-naphthol in the light struck, and hence more conductive, areas of the copysheet surface. When this sheet was then placed in contact with a paper receptor sheet containing silver behenate and heated at 120° C., a positive image was formed on the receptor.

Similar results were achieved with photoconductive copysheets having a coating of carbon black in a butadiene-styrene copolymer matrix (10-20% transmissivity to visible light) instead of vapor coated aluminum. Vapor coated semiconductors, such as p-type InSb, and other materials having relatively low lateral and relatively high transverse electrical conductivity may also be used as top-coatings for the photoconductive layer, provided such layers permit transmission of sufficient radiant energy to activate the underlying photoconductive layer.

EXAMPLE IX

This example illustrates electrolytic masking.

A photoconductive zinc oxide copysheet, as described in Example I, was surface coated with Du Pont Oil Yellow N (Color Index 11020). The copysheet was then exposed to a visible light image, forming a corresponding conductive pattern thereon. With the electrically conductive substrate of the copysheet connected as cathode, electrolytic

development was effected for 3 seconds at 45 volts D.C. using a 3% water dispersion of colloidal alumina (AlOOH) as the electrolytic bath. The positively charged alumina particles deposited selectively on the more conductive areas of the copysheet surface, forming a barrier coating over the yellow dye. This developed sheet was then placed in contact with an ordinary sheet of paper and heated at 250°C . to form a positive dye image on the paper surface.

EXAMPLE X

This example illustrates electrolytic destruction by selective anodic oxidation of a reducing agent.

An aluminum vapor coated photoconductive copysheet, as described in Example VIII, was buffed lightly on the aluminum surface with a 2% solution of hydroquinone in methyl alcohol. After exposure to a light pattern to form a conductive pattern on the copysheet, using the electrically conductive substrate of the copysheet as anode, electrolytic development was effected for three seconds at 40 volts D.C., using a 5% aqueous solution of sodium acetate as the electrolytic bath. This resulted in the selective oxidation of the hydroquinone to quinone on the light struck areas. When this sheet was placed in contact with a paper receptor sheet containing silver behenate and heated at about 120°C ., the vaporized hydroquinone transfers to the receptor and reduces the silver salt to free silver, forming a positive print. When the paper receptor sheet contained red colored 1,3,5-triphenyl formazan, the vaporized quinone oxidized and decolorized the red formazan forming a negative print. If the leuco form of Malachite green (Color Index 4200) is contained in the receptor, the vaporized quinone oxidizes the leuco form to its green colored form, producing a positive print.

Similarly, the copysheet can be coated with quinone and cathodically electrolyzed to form hydroquinone on the light struck areas.

EXAMPLE XI

This example illustrates electrolytic modification by cathodic electrodeposition of an oxidizing agent and the oxidation thereby of a vaporizable reducing agent.

A photoconductive zinc oxide copysheet, as described in Example I, was exposed to a visible light image and electrolytically developed with an aqueous solution containing 3 weight percent $\text{K}_2\text{Cr}_2\text{O}_7$ and 3 weight percent NiCl_2 . The nickel chloride can be replaced with CoCl_2 or MnCl_2 , which also form relatively water insoluble metal chromates. The electrically conductive backing of the copysheet was connected as cathode during electrolysis (40 volts D.C. for about 3 seconds). During cathodic electrolysis the more conductive areas of the copysheet surface become more alkaline, and insoluble nickel chromate precipitates selectively on those surface areas. After the electrolytic step is completed, the copysheet surface is buffed lightly with 4-methoxy naphthol. On those areas having the nickel chromate deposits the 4-methoxy naphthol is oxidized. When the copysheet was placed adjacent a receptor sheet containing silver behenate and heated to about 120°C . for several seconds, the unoxidized 4-methoxy naphthol in the background areas vapor transferred to the receptor and reduced the silver behenate to free silver, forming a positive print.

Other vaporizable reducing agents, such as hydroquinone, can be used in place of the 4-methoxy naphthol to produce similar results. With hydroquinone the oxidation product, i.e., quinone, can also be utilized in conjunction with a receptor sheet containing an oxidizable material, e.g. leuco Malachite green (Color Index 4200).

EXAMPLE XII

This example illustrates electrolytic modification by cathodic electrodeposition of a reducing agent and its reaction with a vaporizable complexing agent.

A photoconductive zinc oxide copysheet, as described in Example I, was top coated by dipping into the following aqueous colloidal sol of a film forming silica containing a vapor transferable reactant.

	Grams
Deionized acid silica sol (34% solids in water; particle size, 16–22 millimicrons, Nalcoag 1034A) _____	50
Water _____	30
Isopropyl alcohol _____	20
Dithiooxamide _____	2

After the top coated copysheet was allowed to dry under ordinary room conditions for several hours, it was exposed to a light pattern and was then cathodically electrolyzed for 1 to 3 seconds (40 volts D.C.) in a 5% aqueous solution of ethyl pyridinium bromide. When the electrolyzed copysheet had dried, it was placed adjacent a paper receptor sheet containing nickel stearate and was heated at about 120°C . for several seconds. A blue positive image was formed on the receptor sheet, the vaporized dithiooxamide from the copysheet background areas reacting with the nickel stearate to form a blue nickel complex. No dithiooxamide transferred from the light struck areas of the copysheet.

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. A process which comprises exposing to activating irradiation a photoconductive, electrolytically developable copysheet having uniformly disposed in the vicinity of the surface thereof a vaporizable image forming material, thereby forming a differential conductivity pattern in said copysheet; electrolytically modifying the vaporizable image forming properties of said material selectively in the more conductive areas of said exposed copysheet by oxidation, reduction, masking or complex formation; then positioning said copysheet adjacent a receptor surface capable of changing color upon contact with said vaporizable image forming material; and uniformly heating said copysheet sufficiently to effect vapor transfer of vaporizable image forming material to said receptor surface, thereby creating a visible image on said receptor surface corresponding to said differential conductivity pattern.

2. The process of claim 1 in which the vaporizable image forming material in the more conductive areas of the photoconductive copysheet is vapor transferred to said receptor surface to create the visible image thereon.

3. The process of claim 1 in which the vaporizable image forming material in the less conductive areas of the photoconductive copysheet is vapor transferred to said receptor surface to create the visible image thereon.

4. The process of claim 1 wherein the vaporizable image forming material is an organic reducing agent.

5. The process of claim 1 wherein the vaporizable image forming material is an organic oxidizing agent.

6. The process of claim 1 wherein the vaporizable image forming property of said vaporizable image forming material is electrolytically destroyed in the more conductive areas of the exposed copysheet.

7. The process of claim 1 in which said receptor surface contains a coreactant which reacts with said vaporizable image forming material to form a product which is more intensely colored than said coreactant.

8. The process of claim 1 in which said receptor surface contains silver behenate and said vaporizable image forming material is a reducing agent for silver behenate.

9. The process of claim 1 in which said receptor surface contains a colored coreactant which reacts with said vaporizable image forming material to form a product which is less intensely colored than said coreactant.

10. The process of claim 1 in which said receptor surface is the surface of a transparent plastic sheet.

11. The process of claim 1 in which said receptor surface is the surface of a paper sheet.

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12. The process of claim 1 wherein the vaporizable image forming property of said vaporizable image forming material is electrolytically modified by electrolytically depositing a masking material thereon.

13. The process of claim 1 wherein the vaporizable image forming property of said vaporizable image forming material is electrolytically modified by electrolytically depositing a polymeric masking material thereon.

14. The process of claim 1 wherein the vaporizable image forming property of said vaporizable image forming material is electrolytically modified by formation of a complex.

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