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PROCESS FOR AUTOELECTROLYTIC REPRODUCTION OF DOCUMENTS

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5 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive autoelectrolytic element is disclosed which includes a backing sheet coated with a mixture of photo-conductive insulating material and a metal having negative electrode potential with respect to hydrogen dispersed in an insulating film forming material. The element is exposed to an image and developed by contact with a solution containing a reducible solute.

This invention relates to electrophotography. More particularly the invention relates to a novel autoelectrolytic process for making photocopies, and to novel photosensitive elements especially adapted for use in the novel process.

The novel elements and novel process can be better understood by comparison with another electrophotographic process called the "photocon" process, which is described, for example, in U.S. Patent No. 3,010,884 patented Nov. 28, 1961, to E. G. Johnson et al.

The photocon process employs a photosensitive element which comprises a photoconductive, electrically insulating coating on an electrically conductive backing. A preferred photoconductive insulating layer for photocon comprises photoconductive zinc oxide dispersed in an insulating resin vehicle. By exposure of this insulating coating, to a light pattern, there is formed a conductive image on photoexposed surface areas on the coating, while unexposed areas remain electrically insulating. An image is then developed on the exposed areas by electrodeposition. A solution of an electrolytic salt, e.g. a silver salt solution, is contacted with the surface of the exposed photoconductive coating while voltage is applied across the photoconductive coating, between the conductive backing as a cathode and the electrolytic solution which contacts the anode and the photoconductive surface. At photoexposed areas the coating is conductive and current across the photoconductive coating causes reduction and electrodeposition of the cation from electrolyte solution. At unexposed areas of the coating there is no current, hence no electrodeposition.

Similarly, the process of the present invention employs an electrophotographic element having a coating that comprises photoconductive particles dispersed in an insulating vehicle on a backing support, and employs an electrolytic solution for development after photoexposure. But the photosensitive element of the present invention is autoelectrolytic, that is, when an electrolyte is applied there is required no externally applied voltage across the photoconductive insulating layer to cause electrolysis.

The novel photosensitive element of my invention comprises a photosensitive autoelectrolytic coating which

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comprises a mixture of photoconductive particles and metal particles dispersed in an insulating vehicle, usually an insulating resin binder.

The novel process of my invention comprises the steps of the first exposing to actinic radiation selected areas on the photosensitive autoelectrolytic element and then applying to the surface of the exposed coating an electrolyte solution containing a solute that will form a visible image by reduction at cathode sites on the photoexposed areas.

Following is a detailed description of a specific example showing a preferred embodiment of the invention.

EXAMPLE I

(A) Preparation of the photosensitive element

To a solution of 4 grams Pilolite A.C. resin in 15 ml. toluene, we add 30 grams of photoconductive zinc oxide and 5 grams of fine zinc filing (2-5 microns diameter), with thorough mixing. We add 100 ml. of toluene and ball mill the mixture for 24 hours. We coat the ball-milled mixture on a paper backing support and dry, first in air then in an oven at 80° C. for several hours to remove residual solvent. The finished element is dark-adapted for several hours prior to photoexposure.

(B) Exposure and development

The coated element is exposed at the coated surface to an actinic light pattern from a 100 watt mercury vapor lamp at a distance of 30 cm. for 8-10 seconds. A developable latent image persists for about two minutes and during this time the exposed element is developed by applying an electrolytic silver solution to the exposed surface. A preferred electrolytic solution consists of

Ammonium bromide	-----gm--	36
Ammonium thiosulfate	-----gm--	2
Silver nitrate	-----gm--	1
Water to make 100 ml.		

To obtain more even development we prefer to prewet the surface by softly rubbing water on the coating just before applying the developer solution. After applying the developer, a silver image develops at the exposed areas in about 5-10 seconds. The element may then be washed with water to remove residual developer and dried. No further fixing or desensitization is necessary.

From the preceding example, it will be seen that the novel photosensitive element and the novel process of the present invention provide a rapid photocopy system of excellent reliability employing relatively inexpensive materials. There is no need in the photosensitive element for a conductive backing, nor is there need in the process for an applied voltage across the photosensitive layer, as are necessary in the photocon process. The novel process is especially adaptable to use in document copying. The results are comparable to those obtained by the photocon process.

The electrochemical phenomenon by which the process of the invention produces a reduced silver image is not entirely understood. Experiments lead us to think the electrolysis proceeds as follows. When a zinc particle in the insulating coating is contacted with electrolytic solution, zinc ions are spontaneously dissolved, leaving negative charge on the zinc particle. In areas made conductive by photoexposure, excess electrons are conducted from

the zinc particle to an adjacent photoconductive zinc oxide particle also in contact with the electrolyte. This conductive zinc oxide particle in turn acts as a cathode providing a reduction site for silver ion. As reduction occurs at the cathode, zinc continues to be dissolved, generates additional ions, and electrolytic deposition proceeds.

My invention is not limited to the preferred example described above. In place of photoconductive zinc oxide in the coating may be substituted other photoconductive insulating particles, for example, photoconductive stannic oxide, cadmium sulfide and the like. Instead of zinc powder I may substitute other metals having negative electrode potential with respect to hydrogen. For example I may use aluminum or magnesium powder. I prefer zinc powder because of its better resistance to surface oxidation which may inhibit the electrolytic activity of the metal particles in the process. Instead of reducible silver ion in the electrolyte I may substitute another reducible cation that is capable when reduced of forming a visible image at the reduction site, for example, silver, gold, tetrazolium, copper, mercury and the like. We prefer to use a complex formed by the metal with a complexing agent. Examples of suitable aqueous electrolytes are 1% KAuCl_4 ; 1% $\text{KAuCl}_4 + 2\%$ thiourea; 0.5% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 1% $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} + 0.5\%$ $\text{Na}_2\text{SO}_3 + 0.35\%$ AgNO_3 ; 0.12% $\text{AgNO}_3 + 0.1\%$ mercaptoethylamine-HCl; 1% 2,3,5-triphenyl-2H-tetrazolium chloride; 0.5% N-methyl-2,4-dinitrobenzyl pyridinium paratoluene sulfonate; 1% molybdic acid, and the like. Also, instead of a reducible silver in the electrolyte I may use a pH-sensitive dye that will form a visible colored precipitate in basic solution. At the photoconductive cathode, electrolysis liberates hydroxyl ion which will reduce and precipitate such dye in the immediate vicinity of the cathode. Thus, reducible dye formers may be employed in the electrolyte instead of reducible silver ion to form a visible image at the photoconductive zinc oxide cathode sites. Suitable indicator dyes for this use include Cotton Blue BB, Aluminum Red B, Lusanne Brilliant Blue B and Methylene Blue Chloride and the like.

To extend the spectral sensitivity of the photosensitive compound I may add sensitizing dyes in minute quantities suitable for the sensitizing function. The sensitizing dyes may be coated on the photosensitive compound before it is mixed with other coating ingredients or it may be added directly in the coating mixture prior to coating. I may use, for example, Rose Bengal, Fluorosecin, Crystal Violet, and the like as sensitizers to extend spectral sensitivity of the photoconductor. A number of other spectral sensitizing dyes for photoconductive zinc oxide are described in the literature, for example in U.S. Patent No. 3,052,540, patented September 4, 1962, by H. G. Greig.

A preferred binder is Pliolite S-7 (a styrene copolymer—Goodyear Tire & Rubber Co., U.S.A.) but other suitable insulating vehicles include 87% vinyl chloride-13% vinylacetate copolymer, Styressol 4444 (a Styrenated alkyd resin, Reichold Chemicals, Inc., U.S.A.), and other insulating, film-forming resins.

The ratio of photoconductive particles to binder in the photosensitive coating is found to influence photographic speed and image density. Increased photoconductor concentration tends to increase speed and density but also tends to increase background development (fog). Operable coatings may contain from about 3 to about 10 parts by weight zinc oxide to one part binder. With Pliolite S-7 we find the optimum ratio of zinc oxide to binder is about 7 to 1. The optimum ratio by weight of zinc oxide to zinc metal in the coatings will depend to some extent on the zinc particle size, purity of the zinc metal and other factors. We prefer to use zinc particles of about 3-5 micron size at a ratio of 1 part by weight zinc to about 6 parts zinc oxide but we may use 1 part zinc to every 3-10 parts zinc oxide.

In addition to zinc or other equivalent metal powder

and zinc oxide or other equivalent photoconductor in the coating, I am also include iron particles. We once thought iron particles were necessary to provide a cathode for the cell but found this is not so.

The backing support for the photosensitive coating may be, but need not be, electrically conductive and we may use any suitable material such as paper, metal foil, resin film, and the like for a support. We prefer a paper support for most purposes. We prefer to apply the coating to the backing by conventional solvent coating methods but extrusion coating or hot melt coating methods can also be adapted for making photosensitive elements of my invention.

It will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

I claim:

1. A photosensitive autoelectrolytic element comprising a backing support and coated thereon a photosensitive layer comprising a physical mixture of discrete particles of photoconductive insulating material and discrete particles of a metal having negative electrode potential with respect to hydrogen dispersed in an insulating film-forming vehicle, there being 3 to 10 parts by weight of photoconductive insulating material for each part by weight of metal and about 3 to about 10 parts by weight of photoconductive insulating material for each part of film-forming vehicle, said layer having the capability after exposure to actinic radiation of spontaneously inducing voltage in an electrolyte sufficient to cause electrolytic reduction at cathode sites in photoexposed areas of said layer.

2. A photosensitive autoelectrolytic element comprising a backing support and coated thereon a photosensitive layer comprising a physical mixture of discrete particles of photoconductive insulating zinc oxide and discrete particles of zinc metal dispersed in an insulating resin film, there being 3 to 10 parts by weight of zinc oxide for each part by weight of zinc and about 3 to about 10 parts by weight of photoconductive insulating material for each part of film-forming vehicle, said layer having the capability after exposure to actinic radiation of spontaneously inducing voltage in an electrolyte sufficient to cause electrolytic reduction at cathode sites in photoexposed areas of said layer.

3. A photosensitive autoelectrolytic element comprising a backing support and coated thereon a photosensitive layer consisting essentially of a physical mixture of photoconductive insulating particles and metal particles dispersed in an insulating film there being 3 to 10 parts by weight of photoconductive insulating particles for each part by weight of metal particles, and about 3 to about 10 parts by weight of photoconductive insulating material for each part of film-forming vehicle, said layer having the capability after exposure to actinic radiation of spontaneously inducing electric voltage in an electrolyte sufficient to cause electrolytic reduction at cathode sites in photoexposed areas of said layer.

4. An electrophotographic process employing a photosensitive autoelectrolytic element, which element comprises a photosensitive layer comprising a physical mixture of photoconductive insulating particles and metal particles dispersed in an insulating film, there being 3 to 10 parts by weight of photoconductive insulating particles for each part by weight of metal particles, and about 3 to about 10 parts by weight of photoconductive insulating material for each part of film-forming vehicle, said layer having the capability, after exposure to actinic radiation, of spontaneously inducing voltage in an electrolyte sufficient to cause electrolytic reduction at cathode sites in photoexposed areas of said layer, said process comprising: (1) exposing selected areas on said photosensitive layer to actinic radiation and (2) applying an electrolytic solution to the exposed layer, said solution containing a solute that is capable of being reduced to

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form a visible image at cathode sites in photoexposed areas of said layer by means of said spontaneously induced voltage.

5. An electrophotographic process employing a photosensitive autoelectrolytic element, which element comprises a photosensitive layer consisting essentially of a physical mixture of photoconductive insulating particles and metal particles dispersed in an insulating film, there being 3 to 10 parts by weight of photoconductive insulating particles for each part by weight of metal particles, and about 3 to about 10 parts by weight of photoconductive insulating material for each part of film-forming vehicle, said layer having the capability, after exposure to actinic radiation, of spontaneously inducing voltage in an electrolyte sufficient to cause electrolytic reduction at cathode sites in photoexposed areas of said layer, said process comprising: (1) exposing selected areas on said photosensitive layer to actinic radiation and

(2) applying an electrolytic solution to the exposed layer, said solution containing a solute that is capable of being reduced to form a visible image at cathode sites in photoexposed areas of said layer by means of said spontaneously induced voltage.

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