⑲ **Europäisches Patentamt**
European Patent Office
Office européen des brevets

⑪ Publication number: **0 034 952**
A2

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: **81300784.6**

㉒ Date of filing: **25.02.81**

(51) Int. Cl.^{3}: **G 03 C 1/02**

㉚ Priority: **25.02.80 US 124189**
05.06.80 US 156712

㊸ Date of publication of application:
02.09.81 Bulletin 81/35

(84) Designated Contracting States:
BE DE FR GB NL

(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester, New York 14650(US)

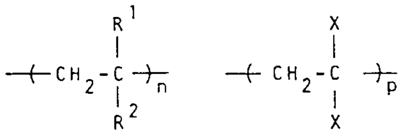
(72) Inventor: **Lelental, Mark**
Kodak Park
Rochester New York(US)

(72) Inventor: **Sutton, Richard Calvin**
Kodak Park
Rochester New York(US)

(74) Representative: **Trangmar, Leigh Alan et al,**
KODAK LIMITED P.O. Box 114 246 High Holborn
London WC1V 7EA(GB)

(54) Heat-developable electrically activatable recording material.

(57) A room light-handleable recording material comprises an electrically conductive support having thereon in sequence (a) a polymeric electrically active conductive (EAC) layer, a recording layer (b) comprising a dye-forming coupler and an oxidation-reduction combination comprising an organic silver salt and a reducing agent having an oxidation product which reacts with the coupler to form image dye. Imagewise passage of current through the material, possibly achieved by applying a potential across the material and an exposed photoconductive layer in contact therewith, produces a heat-developable latent image. Higher current sensitivity of this material is obtained by using as the organic silver salt a salt of a mercapto-1,2,4-triazole derivative and as the polymer for the EAC layer a vinyl addition polymer of the structure:



$$-\!\!\left(\mathrm{CH_2}-\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\mathrm{C}}}\right)_{\!n}\!-\qquad -\!\!\left(\mathrm{CH_2}-\overset{\displaystyle X}{\underset{\displaystyle X}{\mathrm{C}}}\right)_{\!p}\!-$$

wherein R^1 is hydrogen or methyl, R^2 is aryl or R^3COO- where R^3 is alkyl or aryl, each X is bromine or chlorine, and n and p are such that the polymer contains from 50 to 85% by weight of the halogen-containing unit.

./...

EP 0 034 952 A2

Croydon Printing Company Ltd.

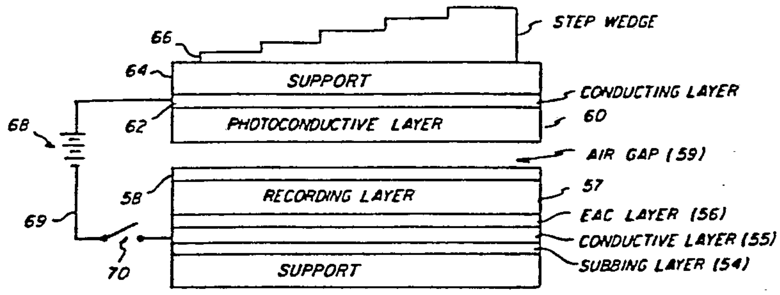

STEP WEDGE
66
64
SUPPORT
CONDUCTING LAYER
68
62
PHOTOCONDUCTIVE LAYER
60
AIR GAP (59)
58
RECORDING LAYER
57
69
EAC LAYER (56)
CONDUCTIVE LAYER (55)
70
SUPPORT
SUBBING LAYER (54)

FIG. 5

HEAT-DEVELOPABLE ELECTRICALLY ACTIVATABLE RECORDING MATERIAL

This invention relates to a heat-developable electrically activatable recording material with which a visible image of dye and silver can be obtained.

In '<u>Research Disclosure</u>', October 1979, Item 18627 there is described a process wherein is used on electrically activatable recording material, this being a sheet material which, when subjected imagewise to an electrical current undergoes a chemical and/or electrical change which provides a developable latent image. In the particular process described, the recording material comprises an electrically activatable recording layer containing a dye-forming coupler and an oxidation-reduction combination comprising a reducible organic silver salt (referred to as an 'organic silver salt oxidizing agent') and a reducing agent having an oxidation product which reacts with the coupler to form an image dye. Passage of current through this material produces a latent image (which may be truly latent or just visible) which can be developed to the desired image of dye and silver by overall heating. It is believed that the latent image consists of silver specks which catalyze the reaction of the oxidation-reduction combination to form silver and oxidized reducing agent, the latter immediately reacting with the coupler to form image dye.

The imagewise passage of current needed for latent image formation can be achieved by a variety of methods. In one of these, the recording layer is maintained in contact with a photoconductive layer (there being an air gap of up to 20 microns thickness in between) and the photoconductive layer is imagewise exposed to produce an imagewise increase in conductivity.

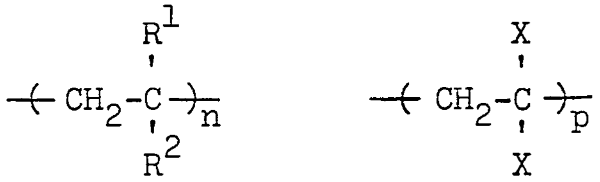
Uniform application of an electrical potential across the layers thereupon provides the desired imagewise pattern of current flow. The electrical potential is conveniently applied by means of two electrically-conductive layers, one behind the photoconductive layer and the other underlying the recording layer and being, or forming part of, an electrically conductive support for that layer.

In the Research Disclosure Item 18627, it is recommended that an electrically conductive subbing layer be provided between the recording layer and the electrically conductive support, this subbing layer possibly comprising an electrically conductive polymer such as poly(alkyl acrylate-co-vinylidene chloride-co-itaconic acid). U.K. Patent Application 2,054,884A suggests that the presence in this position of a polymer layer of this kind (referred to therein an an 'electrically active conductive (EAC) layer') may lead to increased sensitivity of the recording layer, i.e. to a reduction in the amount of current per unit area (the 'charge density') which has to be passed through the layer to form a latent image.

The present invention is based upon the discovery that if a process of the kind described above is carried out using an electrically activatable recording material which comprises a silver salt of a mercapto-1,2,4-triazole derivative, as the reducible organic silver salt, and an electrically active conductive layer formed of a vinyl addition polymer as defined below, then excellent current sensitivity is obtainable.

According to the present invention, there is provided a heat-developable electrically activatable recording material comprising an electrically conductive support having thereon in sequence (a) an electrically conductive polymer layer and (b) a current-sensitive recording layer comprising (A) a dye-forming coupler and (B) an oxidation-reduction combination comprising (i) a silver salt of a mercapto-1,2,4-triazole derivative and (ii) a reducing agent having an oxidation product which reacts with the coupler (A) to form an image dye, characterised in that the layer (a) is an electrically-active conductive layer comprising a vinyl addition polymer composed of two units and of the formula:

(I)



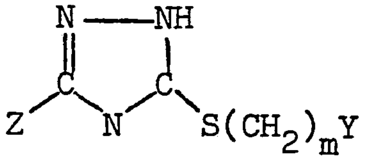
$$-\!\left(CH_2-\overset{R^1}{\underset{R^2}{C}} \right)_n- \qquad -\!\left(CH_2-\overset{X}{\underset{X}{C}} \right)_p-$$

wherein R^1 is hydrogen or methyl, R^2 is aryl, substituted aryl, or $-COOR^3$, wherein R^3 is alkyl, substituted alkyl, aryl or substituted aryl, any aryl group, or aryl residue of any substituted aryl group, containing from 6 to 10 carbon atoms, and any alkyl group, or the residue of any substituted alkyl group containing up to 20 carbon atoms, each X is chlorine or bromine, and n and p are numbers such that the weight percentage of the units I (a) is from 15 to 50 and the weight percentage of the units I (b) is from 85 to 50.

Any alkyl group or residue present in R^2 can be straight chain alkyl and branched chain alkyl. Each alkyl group can be substituted by means of any group that does not adversely affect the desired properties of the electrically activatable recording material such as an oxo group.

The mercapto-1,2,4-triazole derivative is preferably of the formula:

(II)



wherein Y is aryl containing 6 to 12 carbon atoms, m is 0, 1 or 2 and Z is hydrogen, hydroxyl or amine (NH_2). Y may be substituted.

The ohmic resistivity of an electrically conductive support or electrically-active conductive (EAC) layer present in a material of the invention is preferably less than 10^{12} ohm-cm. The preferred ohmic resistivity range for a polymeric EAC layer is 10^4 to 10^{12} ohm-cm.

A dye image and silver image can be produced with a recording material of the invention by a dry process comprising the steps of (I) imagewise applying an electric potential, of a magnitude and for a time sufficient to produce in the image areas of the recording layer a charge density within the range of about 10^{-5} coulomb/cm^2, to about 10^{-8} coulomb/cm^2, thereby forming a developable latent image in that layer; and, then (II) heating the material substantially uniformly at a temperature and for a time sufficient to produce the desired dye and silver image.

A recording material of the invention may comprise a photoconductive layer (c) separated from the recording layer (b) by an air gap of up to 20 micrometres and, behind the photoconductive layer, an electrically conductive layer (d). A dye and silver image may be produced with such a material by a process comprising (I) imagewise altering the conductivity of the photoconductive layer in accord with an image to be recorded;

(II) applying across the photoconductive layer and recording layer an electrical potential of a magnitude and for a time sufficient to produce a developable latent image in the recording layer corresponding to the image to be recorded; and then (III) heating the recording layer substantially uniformly at a temperature and for a time sufficient to produce the desired image. The step (I) of imagewise altering the conductivity of the photoconductive layer is preferably carried out simultaneously with the application of the electrical potential. However, if the photoconductive layer is such that its resistance remains at a lower value for some time following exposure, then the electrical potential may be applied after the imagewise exposure has been made.

Instead of using a photoconductive layer, as just described, the pattern of current flow required to form a latent image can be produced by (I) positioning the electrically activatable material on an electrically conductive backing member; (II) modulating a corona ion current flow to the recording element by an electrostatic field established imagewise between an image grid comprising an electroconductive core sequentially connectable to sources of different potential relative to the backing member and covered with a coating of a photoconductive insulating material and a control grid that is electrically conductive and sequentially connectable to sources of different potential relative to the backing member. .

The heating step in each of the described process embodiments is normally carried out at a temperature within the range of 80°C to 200°C, and preferably at a temperature within the range of 100°C to 180°C.

Figures 1 and 2 illustrate schematically an image recording material and process and Figures 3 and 4 illustrate schematically an electrically activated recording process embodying the described invention.

Figure 5 illustrates schematically an image recording material that is especially useful according to the invention.

The exact mechanism by which the latent image is formed and by which the EAC layer enables increased charge sensitivity in a material according to the invention are not known. It is postulated that the injection of a charge carrier due to the electric field into the combination of components results in the formation of a developable latent image in the electrically activatable recording layer. Some form of interaction which is not fully understood occurs betweeb the current-sensitive recording layer and the EAC layer. The image apparently forms in the exposed areas in the recording layer closest to the interface between the recording layer and the EAC layer, rather than uniformly throughout the exposed areas of the recording layer. It is not clear what part, if any, the dye-forming coupler and the other described components play in latent image formation.

While many image recording combinations containing the described components are useful, the optimum image recording combination and image recording material will depend upon such factors as the desired image, the particular dye-forming coupler, the particular reducible organic silver salt and reducing agent, the source of exposing energy or processing condition ranges.

The vinyl addition polymers useful in an electrically activatable recording material according to the invention are prepared by methods known in the polymer art. The following preparation of poly(methyl acrylate-co-vinylidene chloride) (20:80 weight ratio) is illustrative of methods that are used for preparing such polymers: To a 7.57 litre stainless steel reactor equipped with a stirrer, condenser, baffle and heated jacket is added 4.0 Kg of distilled water and 4.5 g $K_2S_2O_8$. The solution is deoxygenated such as by evacuation four times to boiling with release of pressure using nitrogen gas. The reactor mixture is cooled to 15°C; and 150 grams of surfactant, such as a sodium salt of an alkylarylpolyether sulphate available under the trade mark TRITON 770 from the Rohm and Haas Co., U.S.A., vinylidene chloride (1440 grams) and methyl acrylate (360 grams) are added. Stirring of the reactor contents is maintained throughout the procedure. An additional 200 grams of distilled water containing 2.26 grams of dissolved $Na_2S_2O_5$ is added and the reactor sealed and heated to 35°C. The temperature is maintained at 35°C for 17 hours at a pressure of 170 KPa. The reactor contents are cooled to produce a latex solution of 27.8 percent solids. The polymer is isolated by means of a freeze-thaw technique, washed with distilled water three times using 60 liters of water per wash, centrifuged, and dried at 40°C in vacuum for 17 hours. The resulting polymer has an inherent viscosity in cyclohexane of 0.93 with a Tg of 31°C.

Very suitable polymers are those of formula II for the case where R^2 is $-COOR^3$, R^3 is $-CH_3$ or $-C_2H_5$ and X is chlorine.

Many photoconductors are useful in a material according to the invention. Selection of an optimum photoconductor will depend upon such factors as the particular electrically activatable recording layer, the current sensitivity of the material, the desired image, the ohmic resistivity desired, exposure means, or processing conditions. It is advantageous to select a photoconductor which has the property of being the most useful with the operative voltages to be used for image formation. The photoconductor is either organic or inorganic. Combinations of photoconductors may be used. The resistivity of the photoconductor can change rapidly in the operating voltage ranges that may be used. In some cases, it is desirable that the photoconductive layer have what is known in the art as persistent conductivity. Examples of useful photoconductors include lead oxide, cadmium sulphide, cadmium selenide, cadmium telluride and selenium. Useful organic photoconductors include, for instance, polyvinyl carbazole/trinitrofluorenone photoconductors and aggregate type organic photoconductors described in, for example, U.S. 3,615,414. Photoconductors known in the image recording art are described in, for example, U.S. Patent 3,577,272; <u>Research Disclosure</u>, August 1973, Item 11210 of Reithel; "Electrophotography" by R.M. Schaffert (1975) and "Xerography and Related Processes" by Dessauer and Clark (1965) both published by Focal Press Limited.

An especially useful photoconductive layer comprises a dispersion of a lead oxide photoconductor in an insulating binder, such as a binder comprising a polycarbonate (for example, LEXAN , a trade mark of General Electric Company, U.S.A., consisting of a Bisphenol A polycarbonate), polystyrene or poly(vinyl butyral).

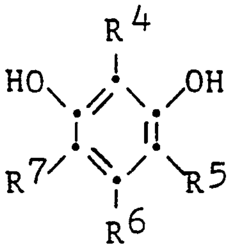
A recording material according to the invention is especially useful wherein the photoconductive layer is X-ray sensitive and the conductivity of the photoconductive layer can be imagewise altered by imagewise exposing the photoconductive layer to X-ray radiation.

Many dye-forming couplers are useful in a material according to the invention. The term dye-forming coupler herein means a compound or combination of compounds which with other of the components produces a desired dye image upon heating the recording layer after exposure. These are designated as dye-forming couplers because it is believed that the compounds couple with the oxidized developer to produce the dye. The dye-forming couplers described herein are also known in the photographic art as color-forming couplers.

Selection of a suitable dye-forming coupler will be influenced by such factors as the desired dye image, other components of the recording layer, processing conditions or particular reducing agent in the recording layer. An example of a useful magenta dye-forming coupler is 1-(2,4,6-trichlorophenol)-3-[3-]α-(3-pentadecylphenoxy)-butyramido [benzamido]-5-pyrazolone. A useful cyan dye-forming coupler is 2,4-dichloro-1-naphthol. A useful yellow dye-forming coupler is α-[3-{α-(2,4-di-tertiary-amylphenoxy) acetamido}-benzoyl]-2-fluoroacetanilide. Useful cyan, magenta and yellow dye-forming couplers can be selected from those described in, for example, "Neblette's Handbook of Photography and Reprography", edited by John M. Sturge, 7th Edition, 1977, pages 120-121 and Research Disclosure, December 1978, Item 17643, Paragraphs VII C-G.

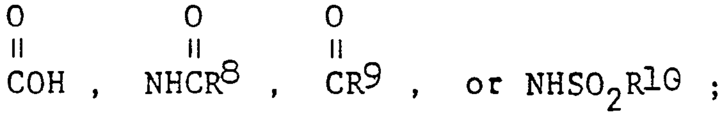
An especially useful dye-forming coupler is a resorcinol dye-forming coupler. The resorcinol dye-forming coupler is preferably one that produces a neutral (black) or nearly neutral appearing dye with the oxidized form of the described reducing agent. Monosubstituted resorcinol dye-forming couplers containing a substituent in the two position are especially useful.

A useful resorcinol dye-forming coupler is one represented by the formula:

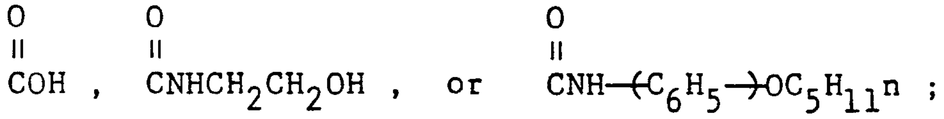


wherein

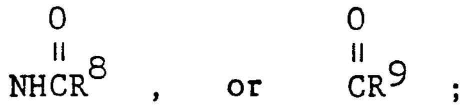
R^4 is hydrogen,


$\overset{O}{\overset{\|}{C}}OH$, $NH\overset{O}{\overset{\|}{C}}R^8$, $\overset{O}{\overset{\|}{C}}R^9$, or $NHSO_2R^{10}$;

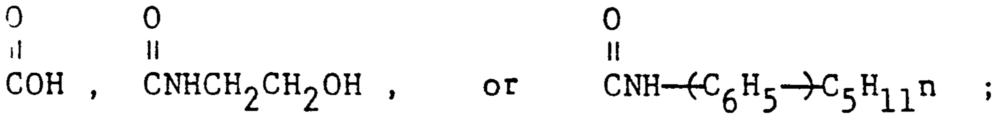
R^5 is hydrogen,


$\overset{O}{\overset{\|}{C}}OH$, $\overset{O}{\overset{\|}{C}}NHCH_2CH_2OH$, or $\overset{O}{\overset{\|}{C}}NH\text{—}(C_6H_5\text{—})OC_5H_{11}n$;

R^6 is hydrogen,


$NH\overset{O}{\overset{\|}{C}}R^8$, or $\overset{O}{\overset{\|}{C}}R^9$;

R^7 is hydrogen,


$\overset{O}{\overset{\|}{C}}OH$, $\overset{O}{\overset{\|}{C}}NHCH_2CH_2OH$, or $\overset{O}{\overset{\|}{C}}NH\text{—}(C_6H_5\text{—})C_5H_{11}n$;

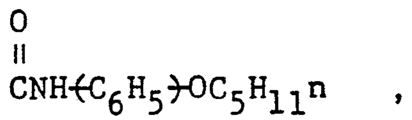
R^8 is haloalkyl containing 1 to 3 carbon atoms, such as CCl_3, CF_3 and $C_3H_4Br_3$, CH_2OCH_3, CH_2SR^{10}, NHR^{11}, C_2H_4COOH, $CH=CH_2$, NHC_2H_4Cl, alkyl containing 1 to 20 carbon atoms or phenyl;

R^9 is OH, NH_2, $NHCH_2CH_2OH$ or $NH(C_6H_5)OC_5H_{11}n$;

R^{10} is alkyl containing 1 to 5 carbon atoms, or phenyl; and

R^{11} is hydrogen, haloalkyl containing 1 to 3 carbon atoms, such as CCl_3, CF_3 or C_3H_4Br, CH_2OCH_3, or C_2H_4COOH.

The letter n, such as in:



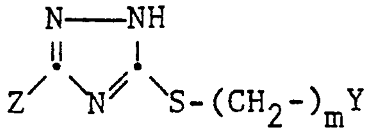
$$\overset{\overset{O}{\|}}{C}NH\!-\!(C_6H_5)\!-\!OC_5H_{11}n \quad ,$$

means normal. Alkyl and phenyl, as described, include alkyl and phenyl that are unsubstituted, as well as alkyl and phenyl that contain substituent groups that do not adversely affect the desired image. An example of a suitable substituent group is alkyl containing 1 to 3 carbon atoms.

Examples of useful resorcinol dye-forming couplers are described in, for example, Research Disclosure, September 1978, Item 17326. Especially useful resorcinol dye-forming couplers include 2',6'-dihydroxyacetanilide and 2',6'-dihydroxytrifluoroacetanilide. Another useful resorcinol dye-forming coupler is 2',6'-dihydroxy-2,5- dimethylbenzanilide (2',6'-dihydroxyacetanilide has also been known as 2,6-dihydroxyacetanilide, and 2',6'-dihydrox-2,5-dimethylbenzanilide has also been known as 2,6-dihydroxy-2',5'-dimethylbenzanilide).

Useful silver salts of 1,2,4-mercaptotriazole derivatives for the invention include those represented by the formula:

(II)



wherein Y is aryl containing 6 to 12 carbon atoms, such as phenyl, naphthyl and para-chlorophenyl; m is 0 to 2; and Z is hydrogen, hydroxyl or amine ($-NH_2$). Especially useful organic silver salts within this class are those silver salts of the described 1,2,4-mercaptotriazole derivatives wherein Y is phenyl, naphthyl or para-chlorophenyl and Z is amine ($-NH_2$). An example of such a compound is the silver salt of 3-amino-5-benzylthio-1,2,4-triazole (referred to herein as ABT). Such organic silver salts are described in, U.S. Patents 4,123,274 and 4,128,557.

Combinations of reducible organic silver salts are useful, such as a mixture of the silver salt of ABT with that of 1-methyl-4-imidazoline-2-thione. Other combinations include a mixture of the silver salt of ABT with a silver salt of a nitrogen acid described in Research Disclosure, Volume 150, October 1976, Item 15026.

Selection of an optimum organic silver salt or organic silver salt mixture will depend upon the described factors, such as the desired image, the particular reducing agent, the particular dye-forming coupler, processing conditions or the particular binder. An especially useful organic silver salt oxidizing agent is the silver salt of ABT.

The term "salt" is used herein in the term "organic silver salt" to refer to a compound comprising any type of bonding or complexing mechanism which enables it to produce desired images in the described recording layer. In some instances, the bonding of the silver with the organic compound is not fully understood. Accordingly, the term "salt" covers, amongst other types of compound, those which are known in the chemical art as "complexes" including neutral complexes and non-neutral complexes.

Many reducing agents which, when oxidized, form a dye with the described dye-forming coupler are useful in the recording material according to the invention. The reducing agent is typically an organic silver halide colour developing agent. Combinations of reducing agents are useful. It is important that the reducing agent produces an oxidized form upon reaction with the organic silver salt which reacts at the processing temperature with the described dye-forming coupler to produce a desired dye. Especially useful reducing agents are primary aromatic amines invluding, for example paraphenylenediamines. The reducing agent may be provided in the recording layer by a precursor compound.

An especially useful type of reducing agent is a paraphenylenediamine silver halide developing agent that exhibits a half-wave potential (E 1/2) value in aqueous solution at pH 10 within the range of -25 to +175 millivolts versus a saturated calomel electrode. This value is determined by analytical procedures known in the photographic art: see, for example, "The Theory of the Photographic Process", 4th Edition, Mees and James, 1977, pages 318-319.

The tone of the combined silver image and dye image produced according to the invention will vary, depending upon such factors as the silver morphology of the developed silver image, the covering power of the silver materials, the particular dye-forming coupler, the particular reducing agent or processing conditions. In recording layers that produce a brown silver image, the hue of the dye image produced is preferably complementary to the hue of the silver image. The hue of the combined dye image and silver image is preferably "neutral", i.e. what is described in the photographic art as blue-black, grey, purple-black or black.

Silica is generally useful in an image recording layer of a recording material according to the invention. Silica in the recording layer helps produce increased density in the heat-developed image. However, colloidal silica is especially useful because it has a large surface area. The optimum concentration of silica in the recording layer will depend upon such factors as the desired image, other components in the recording layer, processing conditions or layer thickness. The preferred concentration of silica is within the range of 1 to 1,000 milligrams per 500 square centimetres of support. The use of silica may be a disadvantage in the preparation of a high resolution transparency, because the silica may reduce resolution of the developed image and cause undesired light scattering.

The average particle size and particle size range of silica in the recording layer will vary. The optimum average particle size and particle size range of silica will depend upon the described factors regarding silica concentration. Typically, the average particle size and particle size range of colloidal silica are most useful. Colloidal silica that is useful includes such commercially available products as "Cab-O-sil" (trade mark) silica available from the Cabot Corporation, U.S.A. and "Aerosil" (trade mark) silica available from DEGUSSA, West Germany. It is important that the average particle size and particle size range of the silica or any other equivalent particles not adversely affect the desired properties of the electrically activatable recording material of the invention or the desired image produced upon imagewise exposure and heating of the recording layer. For instance, the silica selected should not decrease sensitivity of the recording layer or produce undesired fogging of the developed image.

The mechanism and properties which cause colloidal silica to produce increased density in a recording layer according to the invention are not fully understood. It is believed that the large surface area of colloidal silica contributes to the desired results. In any case, an especially useful embodiment of the invention, as described, is one containing colloidal silica in the recording layer of a charge-sensitive recording material according to the invention.

The electrically activatable recording layer in a material of the invention preferably contains a binder, which is chosen to give the desired electrical resistivity and is preferably an electrically conductive polymeric binder.

The electrically activatable recording material according to the invention may comprise any of a variety of supports. The term "electrically conductive support" herein includes (a) supports that are electrically conductive without the need for separate addenda in the support or on the support to produce the desired degree of electrical conductivity and (b) supports that comprise addenda or separate electrically conductive layers that provide the desired degree of electrical conductivity. Typical supports include cellulose ester, poly(vinyl acetal), poly(ethylene terephthalate), polycarbonate and polyester film supports and related films and resinous materials. Other supports are useful, such as glass, paper, metal and the like which can withstand the processing temperatures described and do not adversely affect the charge-sensitive properties and ohmic resistivity which is desired. A flexible support is most useful. It is necessary that the various layers according to the invention adhere to the support. A subbing layer to aid adhesion is preferred on the support. Such a subbing layer is, for example, a poly(methyl acrylate-co-vinylidene chloride-co-itaconic acid) subbing layer.

The recording material according to the invention generally includes an electrically conductive layer positioned between the support and the described polymeric EAC layer. This is illustrated by electrically conductive layer 55 in Figure 5. The electrically conductive layers, as described, such as layers 62 and 55 in Figure 5, comprise a variety of electrically conducting compounds which do not adversely affect the charge sensitivity and ohmic resistivity properties of an element according to the invention. Examples of useful electrically conductive layers include layers comprising an electrically conductive chromium composition, such as cermet, and nickel.

In some embodiments, the photoconductive layer is a self-supporting layer, such as a photoconductor in a suitable binder. In such embodiments an electrically conductive layer, such as an electrically conductive nickel or chromium composition layer, is coated on the photoconductive layer. This is illustrated in, for instance, Figure 3 in the drawings in which electrically conductive layer 28 is on photoconductive layer 30 which is self-supporting. Alternatively, the photoconductive layer is coated on an electrically conductive support, such as illustrated in Figure 5 of the drawings.

Useful electrically activatable materials according to the invention comprise an electrically conductive support having thereon a current-sensitive recording layer which has a thickness preferably within the range of 1 to 30 microns, and more preferably within the range of 2 to 15 microns. The optimum layer thickness of each of the layers of a material according to the invention will depend upon such factors as the particular ohmic resistivity desired, current sensitivity, particular components of the layers and the desired image.

The polymeric EAC layer, such as layer 56 illustrated in Figure 5, preferably has a thickness within the range of 0.02 to 10 microns, and more preferably within the range of 0.05 to 5 microns. The optimum layer thickness of the polymeric electrically conductive EAC layer of a material according to the invention will depend upon such factors as the particular ohmic resistivity desired, the current sensitivity, the kind of image desired and the composition of the electrically activatable recording layer.

The optimum concentration of the described components of a material according to the invention will depend upon a variety of factors. An especially useful recording material according to the invention comprises 1 to 5 moles of the dye-forming coupler for each 1 to 5 moles of the reducing agent and 3 to 20 moles of the reducible organic silver salt.

The ratio of the organic moiety to silver ion in the organic silver salt oxidizing agent can have a range of values, the optimum value depending upon such factors as the particular organic moiety, the particular concentration of silver ion desired, the processing conditions, and the particular dye-forming coupler. The molar ratio of organic moiety to silver as silver ion in the salt is typically within the range of 0.5:1 to 3:1.

The image recording layer of the invention may have a range of pAg values. The pAg is measured by means of conventional calomel and silver-silver chloride electrodes, connected to a commercial digital pH meter. The pAg in a dispersion containing the described components for the recording layer is advantageously within the range of 2.5 to 7.5. The optimum pAg will depend upon the described factors, such as the desired image and the processing conditions.

A recording layer containing the desired organic silver salt typically has a pH value of from 1.5 to 7.0. An especially useful pH value is within the range 2.0 to 6.0.

The desired resistivity characteristics of a recording layer according to the invention is obtained by separately measuring the current-voltage characteristic of each sample coating at room temperature by means of a mercury contact sample holder to make a mercury contact to the surface of the coating. To eliminate the possibility that a micro thickness surface air gap might affect the measured resistivity, exposures are made with evaporated metal (typically, bismuth or aluminium) electrode on the surface of a charge sensitive coating to be tested. The resistivity is measured at various ambient temperatures. The data are measured at a voltage of, for example, 20 volts or 4 x 10^4 volts per centimetre, which is within the ohmic response range of the layer to be tested. The resistivity of the charge-sensitive layer will vary widely with temperature. The dielectric strength of the layer will also vary with temperature.

An especially useful embodiment of the invention having the desired characteristics comprises an electrically activatable recording material preferably having an ohmic resistivity of at least about 10^4 ohm-cm, comprising, in sequence: (a) a first electrical conducting layer, (b) a photoconductive layer, (c) an electrically activatable recording layer separated from (b) by an air gap of up to about 20 microns and comprising, in reactive association: (A) the dye-forming coupler 2',6'-dihydroxy trifluoroacetanilide, (B) an image-forming combination containing (i) a silver salt of 3-amino-5-benzylthio-1,2,4-triazole, with (ii) the reducing agent aniline sulphate, and (C) a poly-acrylamide binder, (d) an EAC layer of a poly(alkyl acrylate-co-vinylidene chloride) on (e) a second electrical conducting layer, such as cermet layer, on (f) a support, such as a support having a subbing layer comprising poly(methyl acrylate-co-vinylidene chloride-co-itaconic acid).

A variety of energy sources are useful for imagewise exposure of a recording material according to the invention. Selection of an optimum energy source for imagewise exposure will depend upon the described factors, such as the sensitivity of the photoconductor layer, the particular image recording combination in the current-sensitive recording layer, and the desired image. Useful forms of energy for imagewise exposure include, for example, visible light, X-rays, laser radiation, electron beams, ultraviolet radiation, infrared radiation and gamma rays.

An especially useful process embodiment of the invention is a dry electrically activatable recording process for producing a dye enhanced silver image in an electrically activatable recording material, preferably having an ohmic resistivity of at least about 10^4 ohm-cm, comprising, in sequence, a support having thereon (a) a first electrically conductive layer, (b) an organic photoconductive layer, (c) an electrically activatable recording layer separated from (b) by an air gap of up to 20 microns and comprising (A) a dye-forming coupler which is 2',6'-dihydroxyacetanilide or 2',6'-dihydroxytrifluoroacetanilide or a mixture thereof, (B) an image-forming combination comprising (i) a silver salt of 3-amino-5-benzylthio-1,2,4-triazole, with (ii) the reducing agent 4-amino-2-methoxy-N,N,5-trimethylanilinesulphate, and (c) a polyacrylamide binder, (d) a polymeric EAC layer according to the invention and (e) a second electrically conductive layer; said process comprising the steps: (I) imagewise altering the conductivity of the photoconductive layer in accord with an image (X') to be recorded while simultaneously (II) applying across the photoconductive layer and recording layer an electrical potential of a magnitude and for a sufficient time to produce a developable latent image in the recording layer corresponding to the image (X'); and then (III) heating the recording layer substantially uniformly at a temperature and for a time sufficient to produce a dye enhanced silver image corresponding to image (X') in the recording layer.

In producing an image by a method of the invention an imagewise current flow is produced through the described electrically activatable recording layer. The preferred techniques for producing this current flow are those which include use of a photoconductive layer as an image to current converter. If desired, however, the imagewise current flow may be provided by contacting the recording material with electrostatically charged means, such as an electrostatically charged stencil or by scanning the recording material with a beam of electrons.

Heating the recording material after latent image formation is carried out by techniques and by means known in the photothermographic art. For example, the heating is carried out by passing the imagewise exposed recording material over a heated platen or through heated rolls, by heating the material by means of microwaves, by means of dielectric heating or by means of heated air. A visible image is produced in the described exposed material within a short time, that is within about 1 to about 90 seconds, by the described uniform heating step. An image having a maximum transmission density of at least 1.0 and typically at least 2.2 can be produced according to the invention. For example, the recording material is uniformly heated to a temperature within the range of about 100°C to about 200°C until a desired image is developed, typically within 1 to 90 seconds. The imagewise exposed material according to the invention is preferably heated to a temperature within the range of 120°C to 180°C. The optimum temperature and time for processing will depend upon such factors as the desired image, the particular recording material or heating means.

The described electrically activatable recording process is useful for producing multiple copies. According to this embodiment of the invention, multiple copies are prepared by (I) imagewise altering the conductivity of a photoconductive layer in accord with an image that is to be recorded; (II) positioning the imagewise altered photoconductive layer from (I) adjacent to a current sensitive recording layer of the recording material, (III) applying an electrical potential across the photoconductive layer and recording layer of a magnitude and for a time sufficient to produce in the areas of the recording layer corresponding to the imagewise altered portions of the photoconductive layer a charge density within the range of about 10^{-5} coulomb/cm^2 to about 10^{-8} coulomb/cm^2, the charge density forming in the areas a developable latent image; then (IV) uniformly heating the recording material at a temperature and for a time sufficient to produce a dye image and silver image in the recording material;

followed by (V) positioning the imagewise altered photoconductive layer adjacent another current-sensitive recording layer and repeating the steps (III) and (IV) to produce a further copy.

The reducible organic silver salt, reducing agent and coupler must be located with respect to each other in such a way that the nuclei formed on current exposure can catalyze the reduction of the silver salt, and so cause formation of the dye and silver image. The organic silver salt, reducing agent, and dye-forming coupler must therefore be in what may be termed 'reactive association' in the electrically activatable recording material.

Referring to the drawings, one embodiment of the invention is depicted schematically in Figures 1 and 2. As shown in these Figures, an electrically-activatable recording layer 10 having a polymeric EAC layer 11 according to the invention is placed upon a grounded electrically conductive backing or support 12. A current is selectively applied to the recording layer 10 by the point of a metal stylus 14 which is raised to a sufficiently high voltage relative to the support 12 by a voltage source 16, and brought into moving contact with the exposed surface of the recording layer 10 containing the described image-forming combination and dye-forming coupler. Upon contacting the recording layer 10 with the stylus 14, a current flow is produced in the areas, such as area 18, of the recording layer contacted by the stylus and a developable latent image forms, i.e. a pattern of nuclei sites, in the pattern desired. The charge density produced by the stylus in the contacted areas of the recording layer must be sufficient to produce a latent image in the recording layer in those areas contacted by the stylus, this latent image possibly being just visible. The area of the recording layer 10 designated as 18 contains a latent image of nuclei formed upon contact of the stylus 14 with the recording layer 10. Other techniques for producing a nuclei pattern include, for example, contacting the recording layer 10 with an electrostatically charged stencil or scanning the layer 10 with a beam of electrons in an image pattern.

Figure 2 illustrates development of the latent image formed in the recording material in Figure 1 by, for example, moving the material from Figure 1 into contact with a heated metal platen 24. The heat from platen 24 passes through the support 22 and polymeric EAC layer 21 according to the invention to the layer 20 containing the latent image to cause the desired reaction in the latent image area. The reaction in the latent image area causes development to produce a visible image 26 consisting essentially of dye and silver in the recording layer 20. Upon development the recording material is removed from the platen 24. No processing solutions or baths are required in this heat development step.

Another illustrative embodiment of the invention is schematically shown in Figures 3 and 4. In this embodiment, in Figure 3, the developable sites 40 and 42, that is the latent image sites, are formed by sandwiching an electrically activatable recordin layer 32 and an image-to-current converter layer 30, preferably a photoconductive layer, between a pair of electrically conductive layers 28 and 34. A polymeric EAC layer 33 according to the invention is present between electrically conductive layer 34 and current-sensitive recording layer 32. Layers 28 and 34 comprise, if desired, suitable supports for layers 30, 32 and 33 or layers 28 and 34 are on separate suitable supports, not shown, such as film supports. A high potential electric field, such as at a voltage within the range of 0.01 to 6.0 KV, is established across the photoconductive layer 30 and recording layer 32 by connecting the conductive layers 28 and 34 by connecting means 35 containing power source 36. The electric field across the layers is controlled by switch 38. The latent image formation at latent image sites 40 and 42 is caused by imagewise exposing the photoconductive layer 30 through the conductor 28 to exposure means 44, typically actinic radiation, preferably X-ray. The layer 28 and any support for conductive layer 28 must be sufficiently transparent to the energy 44 to enable the energy to pass to a desired degree to photoconductive layer 30. The exposure selectively increases the conductivity of the conductive layer in those regions exposed to actinic radiation. When switch 38 is closed thereby establishing an electric field across the layers, an imagewise current flow is produced through the recording layer 32. The current flow occurs in those regions of the recording layer 32 adjacent to the exposed portions of the photoconductive layer 30. An air gap 46 of up to 20 microns is provided between layers 30 and 32. The air gap 46 is, for example, 1 to 10 microns. After a sufficient charge density, typically less than 1 millicoulomb per square centimeter, preferably about 1.0 microcoulomb/cm^2, has been produced in the current exposed portions of the recording layer 32, switch 38 is opened, thereby disrupting the current flow.

The described technique for application of voltage across the photoconductive and recording layers is illustrative. A variety of techniques known in the recording art are useful and are intended to be included in this description. For example, a grid controlled corona exposing means, not shown, such as described in U.S. Patent 3,370,212, can be substituted for the voltage source and conductive layer 28.

To develop the dye image and silver image in latent image sites 40 and 42, the recording material containing layers 32, 33 and 34 is moved away from the photoconductive layer 30. Connecting means 35 is also disconnected. The recording material illustrated in Figure 4 is then contacted with a heating means, such as a heated platen 52 illustrated in Figure 4. The heat from the platen 52 passes through the support 50 and polymeric EAC layer 47 to the layer 48 containing a latent image to produce a visible dye image and silver image 49. The heating is preferably carried out substantially uniformly by merely positioning the recording element in heat transfer relationship with the heated platen 52. After the development of the silver image and the dye image, the recording material is removed from the platen.

An especially useful embodiment of the invention is illustrated in Figure 5 in the drawings. In Figure 5, the electrically activatable recording material consists of a support 53 having thereon a polymeric subbing layer 54, such as a poly(alkyl acrylate-co-vinylidene chloride-co-itaconic acid) subbing layer, having thereon an electrically conductive layer 55, typically consisting of a cermet composition, having thereon a polymeric EAC layer 56. The subbing layer 54 helps the conductive layer 55 adhere to the support 53. On the polymeric EAC layer 56 is coated a recording layer 57 containing the image-forming combination and dye-forming coupler. An air gap 59, such as up to 20 microns, is present between overcoat layer 58 on recording layer 57 and a lead monoxide photoconductive layer 60. Photoconductive layer 60 has a nickel electrically conductive layer 62 which is on a transparent film support 64. Developable nuclei are formed in recording layer 57 by imagewise exposure with a suitable radiation source, such as a tungsten light source or X-ray source, not shown, through step tablet 66. At the time of imagewise exposure with the energy source, a high potential electric field, such as at a voltage within the range of 0.01 to 6.0 KV, is established across the photoconductive and image-recording layers by connecting the conductive layer 62 and the electrically conductive layer 55 by connecting means 69 through a power source 68. The electric field across the layers is controlled by switch 70. After the necessary charge density is established, switch 70 is opened, thereby disrupting the current flow. Imagewise exposure for about 1 second at about 538 lx produces ~~a~~ developable image in recording layer 57. A 0.3 density step wedge is used for imagewise exposure purposes if desired. To develop the resulting latent image, layer 57 is disconnected from connecting means 69 and power source 68 and moved away from the photoconductive layer 60. The recording layer 57 is then heated uniformly by contacting it with a heated metal platen, not shown, until the desired dye image and silver image are produced.

The photoconductive layer, such as the layer 60 in Figure 5, can include a variety of binders and/or sensitizers known in the electrophotographic art. Useful binders are described in, for example, U.S. Patents 2,361,019 and 2,258,423. Sensitizing compounds useful in the photoconductive layer are described in U.S. Patent 3,978,335 .

In the embodiments illustrated which use an air gap between the photoconductive and image recording layers, the air gap distances are controlled by methods known in the art, such as by the roughness of the surface of the photoconductive layer, as well as the roughness of the surface of the image recording layer. The air gap need not be uniform. However, best results are often observed with a uniform air gap. The air gap is for example, up to about 20 microns thick. For example, the distance shown in Figure 3 between photoconductive layer 30 and recording layer 32 is up to 20 microns, as illustrated by air gap 46.

The resistivity of a useful recording layer according to the invention can be affected by air gap effects. The number of variables affecting the resistance of the recording layer can affect the choice of an optimum recording material and imaging means. The resistivity values as described herein for particular recording materials are values measured under optimum temperature conditions during exposure.

If desired, the recording material and image-forming means according to the invention are readily modified to provide a continuous image recording operation. This is carried out by means of desired control circuitry and continuous transport apparatus, not shown.

The following examples are included for a further understanding of the invention.

Example A

This is a comparative example.

This illustrates a negative-working electrically activatable recording material and process for producing a dye image and silver image.

The material and layers for this example are similar to those described in Figure 5, with the exception that the layer 56 did not consist of a polymeric EAC layer according to the invention. Layer 56 in this example consisted of poly(methyl acrylate-co-vinylidene chloride-co-itaconic acid) (15:83:02 ratio).

The following composition (A) was coated on an electrically conductive support. This support consisted of a poly(ethylene terephthalate) film support containing a poly(methyl acrylate-co-vinylidene chloride-co-itaconic acid) (15:83:02 ratio) subbing (layer 54) layer having thereon a Cermet conducting layer and over that a layer 56 of the polymer used for the subbing layer.

Composition (A):

silver 3-amino-5-benzylthio-1,2,4-triazole (1.5:1 ligand to silver ion ratio) (dispersed in 1 percent gelatin)(organic silver salt oxidizing agent)	16.0 ml

methyl mercaptotriazole (1% solution in ethanol) (antifoggant)	0.6 ml
4-phenyl-3-imino-5-thiourazole (1% solution in ethanol) (development accelerator)	0.6 ml
surfactant (Surfactant 10G which is a polyglycidol ether available from the Olin Corporation, U.S.A.) (10% solution in water)	0.2 ml
4-amino-methoxy-N,N,5-trimethyl aniline sulphate (reducing agent)	75 mg (dissolved in 1 ml of water)
2',6'-dihydroxytrifluoroacetanilide (dye-forming coupler)	128 mg (dissolved in 1 ml of water
poly(acrylamide-1-vinylimidazole) (90:10 ratio) (5.6 percent by weight solution in water) (binder)	1.0 ml

The composition after mixing was coated at a 12 mil wet coating thickness to produce a recording layer (57 in Figure 5) containing 100 to 120 milligrams of silver per 929 cm^2 of support.

The layer 60 consisted of a 17 micron thick coating of a composite type organic photoconductor consisting essentially of an aggregate organic photoconductor as described in U.S. 3,615,414 as the photoconductive compound. The photoconductor was coated on conducting layer 62 consisting of copper iodide on a poly(ethylene terephthalate) film support 64 shown in Figure 5. An air gap of up to 20 microns separated the photoconductive layer 60 from recording layer 57. Visible light exposure imagewise was made with simultaneous application of a voltage of positive 4,000 volts to the resulting structure shown in Figure 5. The intensity and duration of light exposure were sufficient to produce a developable latent image in the recording layer 57. A charge exposure of 2.4 microcoulombs/cm^2 was used for forming a latent image in the recording layer 57. This level of charge exposure was necessary to provide a developed image density of 1.0.

The photoconductive layer and the recording layer were separated after imagewise exposure and the recording layer was uniformly heated for 10 seconds at 180°C. This produced a silver image and dye image in the exposed areas of the recording layer. A 1.0 transmission density image was observed in the area exposed to charge.

Example 1

This example illustrates the invention.

An electrically activatable recording material was prepared as described in Example A with the exception that the layer 56 was a poly(methyl acrylate-co-vinylidene chloride) (20:80 weight ratio) EAC layer. This layer was coated on the cermet layer at 1.33 ml per 929 cm^2 of support from a 1.5 percent by weight solution of the polymer in methyl ethyl ketone.

A charge exposure of 1.0 microcoulomb/cm^2 was necessary to produce a developed image having a maximum transmission density of 1.0.

This illustrates that a material according to the invention requires significantly less charge exposure to obtain a developed image having a desired maximum density than the comparison material described in the foregoing Example A.

Examples 2-5

Electrically activatable recording materials were prepared as described in Example 1 with the exception that EAC layer (56) was a poly(methylacrylate-co-vinylidene chloride) polymer having the monomer weight ratio as indicated in the following Table:

Table

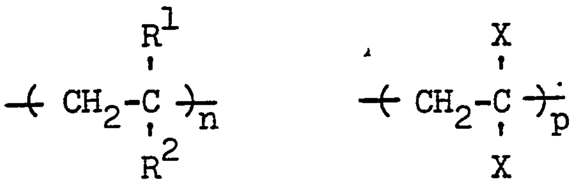
Example No.	Methylacrylate: Vinylidene Cl ratio	Charge Exposure, microcoulombs/ cm^2	Dmax/ Dmin
2	5:95	10.0	1.0/0.22
3	10:90	10.0	1.0/0.22
4	15:85	1.5	1.0/0.22
5	30:70	1.5	1.0/0.22

In each example the EAC layer was coated on a cermet layer, as described in Example A, at 1.33 ml per 929 cm^2 of support from a 1.5 % by weight solution of the polymer in methyl ethyl ketone. The charge exposure required to produce a developed image having a maximum transmission density of 1.0 is indicated in the Table.

CLAIMS

1. A heat-developable electrically activatable recording material comprising an electrically conductive support having thereon in sequence (a) an electrically conductive polymer layer, and (b) a current-sensitive recording layer comprising (A) a dye-forming coupler and (B) an oxidation-reduction combination comprising (i) a silver salt of a mercapto-1,2,4-triazole derivative and (ii) a reducing agent having an oxidation product which reacts with the coupler (A) to form an image dye, characterised in that the layer (a) is an electrically-active conductive layer comprising a vinyl addition polymer composed of two units and of the formula:

(I)



$$-\!\left(\mathrm{CH_2}-\overset{R^1}{\underset{R^2}{C}}\right)_n- \qquad -\!\left(\mathrm{CH_2}-\overset{X}{\underset{X}{C}}\right)_p-$$

wherein R^1 is hydrogen or methyl; R^2 is aryl, substituted aryl, or $-COOR^3$, wherein R^3 is alkyl, substituted alkyl, aryl or substituted aryl, any aryl group, or the aryl residue of any substituted aryl group, containing from 6 to 10 carbon atoms, and any alkyl group, or the residue of any substituted alkyl group containing up to 20 carbon atoms, each X is chlorine or bromine, and n and p are numbers such that the weight percentage of the units I (a) is from 15 to 50 and the weight percentage of the units I (b) is from 85 to 50.

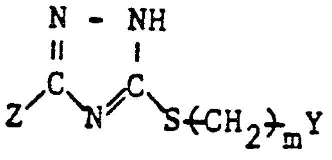
2. An electrically activatable recording material according to Claim 1 comprising (c) a photoconductive layer separated from the current-sensitive recording layer (b) by an air gap of up

20 micrometres and, behind the photoconductive layer, an electrically conductive layer (d).

3. An electrically activatable recording material according to Claim 1 or 2 wherein the electrically active conductive layer is formed of a polymer represented by the formula I of Claim 1 for the case where R^2 is $-COOR^3$, R^3 is $-CH_3$ or $-CH_2CH_3$ and X is chlorine.

4. An electrically activatable recording material according to any of Claims 1 to 3 wherein the polymeric electrically active conductive layer is from 0.02 to 10 microns in thickness.

5. An electrically activatable recording material according to any of the preceding Claims wherein the mercapto-1,2,4-triazole derivative is represented by the structure:



wherein Y is aryl containing 6 to 12 carbon atoms, which may be substituted; m is 0 to 2; and Z is hydrogen, hydroxyl, or amine (NH_2).

6. An electrically activatable recording material according to any of the preceding Claims wherein the electrically conductive support comprises a poly(ethylene terephthalate) film having thereon, in sequence, a subbing layer and an electrically conductive cermet layer.

7. An electrically activatable recording material according to any of the preceding Claims wherein the electrically activatable recording layer also comprises an electrically conductive polymeric binder.

8. A method of making a visible image which comprises passing electric current imagewise through the recording layer of an electrically activatable material according to any of the preceding Claims so as to form a latent image therein and heating the layer overall to develop the latent image to a visible image of dye and silver.

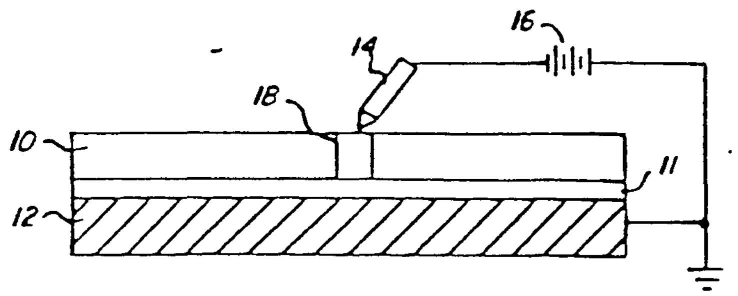


FIG. 1

LATENT IMAGE
FORMATION

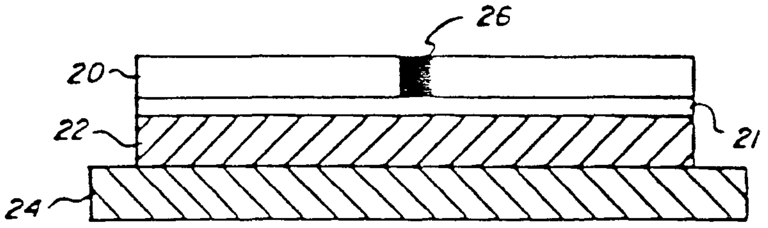


FIG. 2

HEAT DEVELOPMENT

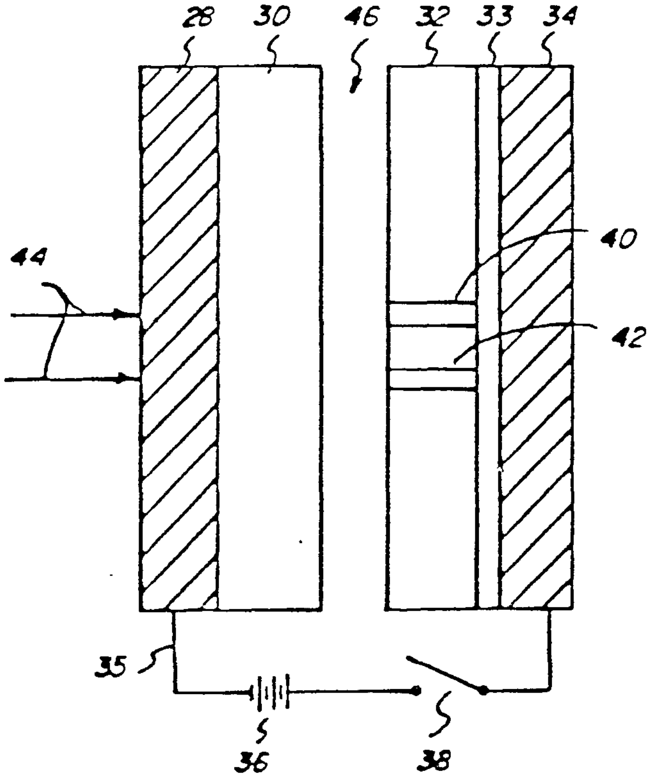


FIG. 3

LATENT IMAGE
FORMATION

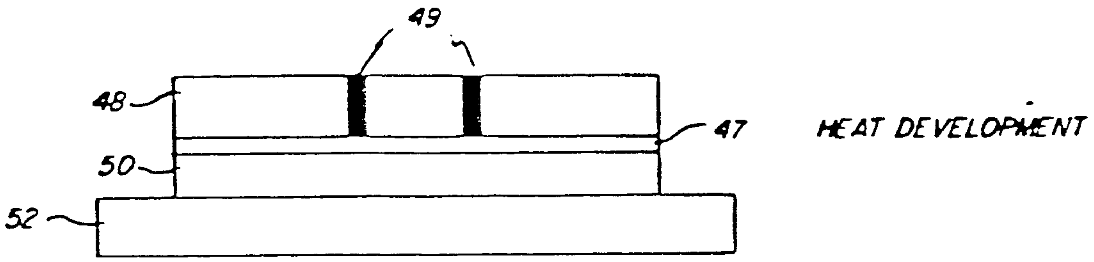

49
48
47
HEAT DEVELOPMENT
50
52

FIG. 4

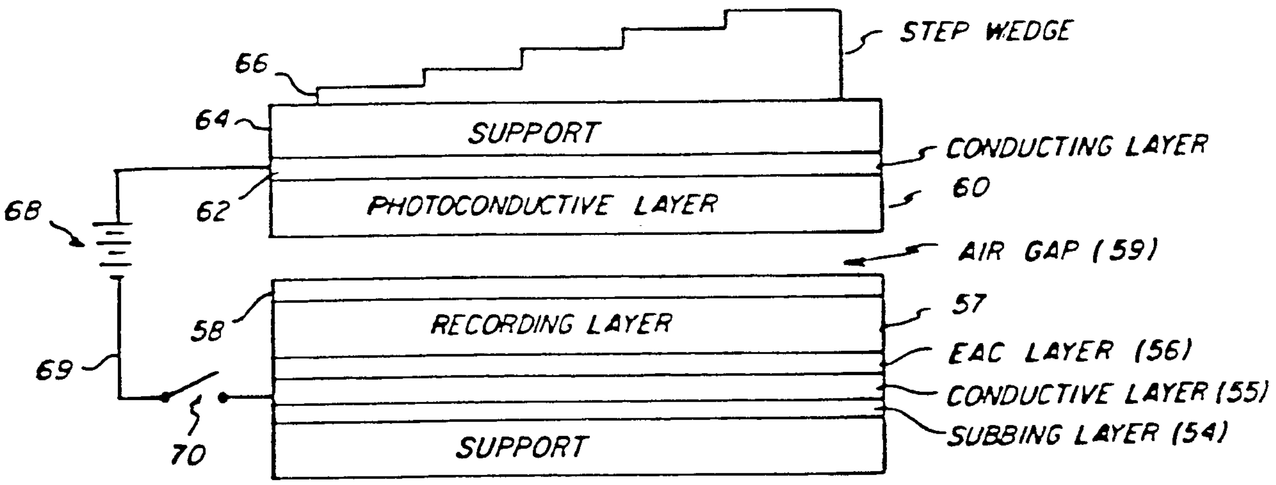

STEP WEDGE
66
64
SUPPORT
CONDUCTING LAYER
62
PHOTOCONDUCTIVE LAYER
60
68
AIR GAP (59)
58
RECORDING LAYER
57
EAC LAYER (56)
69
CONDUCTIVE LAYER (55)
SUBBING LAYER (54)
70
SUPPORT

FIG. 5