Jan. 8, 1963 D. L. JOHNSON ET AL 3,072,542

SINGLE STEP DIRECT IMAGE FORMING ELECTROLYTIC DEVELOPER FOR PHOTOCONDUCTOGRAPHIC PROCESSING

Filed June 14, 1961

Fig. 1

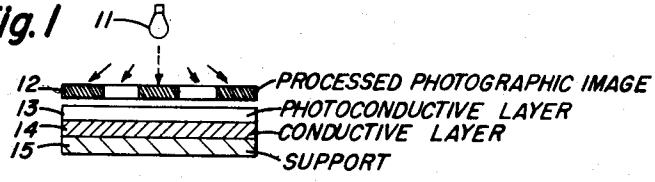


Fig. 2

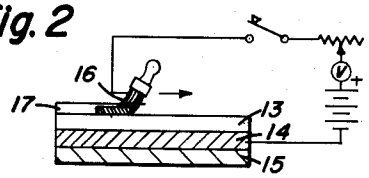


Fig. 3

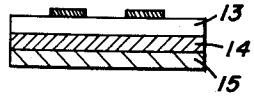
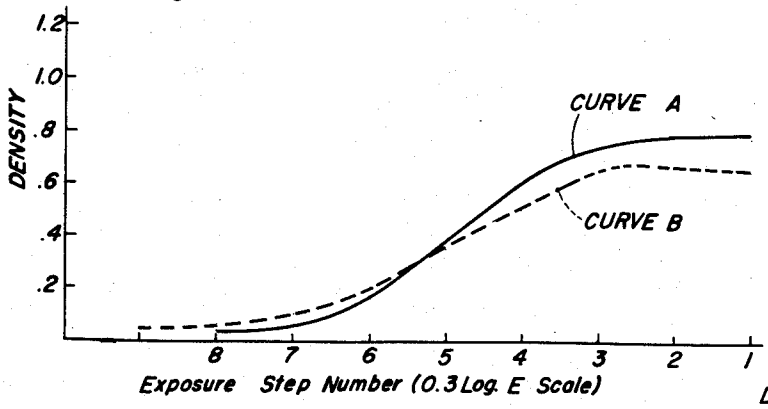


Fig. 4



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United States Patent Office 3,072,542 Patented Jan. 8, 1963

3,072,542

SINGLE STEP DIRECT IMAGE FORMING ELECTROLYTIC DEVELOPER FOR PHOTOCONDUCTOGRAPHIC PROCESSING

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Filed June 14, 1961, Ser. No. 117,125
16 Claims. (Cl. 204—18)

This invention relates to photoconductography and more particularly to a novel developer solution for single-step direct image-forming photoconductographic processing.

Photoconductography is the process of producing images by using photoelectrically sensitive materials to control the electrolytic deposition or formation of a material capable of being the image or capable of being converted to the image by other means. It forms a complete image at one time or at least a nonuniform part of this image as is distinguished from facsimile which at any one time produces only a uniform dot.

Photoconductography is described in detail in British Patent 188,030, Van Bronk, and British Patent 464,112, Goldman, modifications being described in British 789,309, Berchtold, and Belgian 561,403, Johnson et al.

The present invention is concerned with those processes of photoconductography in which the production of the image is brought about by a single-step direct image-forming electrolytic developer. Single-solution or single-step electrolytic developers used in this process are to be distinguished from those developers in which the electrolytic deposition or formation of a faintly visible image material is subsequently made visible by a second step, which may be chemical, electrical, or mechanical. Single-solution electrolytic developers are those developers which will produce a useful visible image material by a single electrolytic development step and require no further treatment for image formation. The present invention pertains to processes of photoconductography in which the image is formed simultaneously with exposure of the photoconductive layer or in which the image is developed after exposure has terminated. (See Franz Urbach U.S. application Serial No. 64,901, filed October 25, 1960.)

The present invention also pertains to processes of photoconductography without regard for the particular method used for bringing about development of the image. For example, widely diverse techniques can be employed in development to apply and distribute the developer solution over the photoconductive layer of the photoconductographic material, such as the use of an angular sweeping blade for distributing the electrolytic developer as provided by an automobile windshield wiper, a viscose sponge containing developer solution, a transfer roller covered with developer solution, a rotary brush containing developer solution, etc. Another suitable technique involves distributing the electrolytic developer over the surface of the print-forming layer in the area between a surface transparent electrode and the photoconductive layer.

The present invention provides an electrolytic developer which can be employed for image development in processes of photoconductography where a wide variety of photoconductive layers are employed. For example, the photoconductive layers can comprise zinc oxide or other suitable light colored photoconductors in a suitable insulating resinous binder. The photoconductive layers can also contain sensitizing dyes or other sensitizing materials in which a higher level and range of sensitivity is obtained in a given spectral region or spectral sensitization can be brought about in more than one spectral region.

Silver nitrate, thiourea-silver complexes, and thiosulfate-silver complexes have been used in electrolytic developers. These developers, however, have had various disadvantages. Silver nitrate in particular, as well as some of the silver complex developers known previously, have had poor keeping qualities. For example, developers based on thiosulfate-silver complexes have a normal storage life of only about one week. Some of these developers are characterized by strong oders, which are not only unpleasant to the person using the developer, but may be unpleasant to the person using the prints produced with them. Some of the prior art developers are characterized by reacting chemically with the zinc oxide, especially in the presence of light, after electrolytic processing and, therefore, must be thoroughly removed to avoid printout. Silver nitrate developers, for example, when left on the photoconductor surface after processing, will produce very serious printout after only 10 seconds exposure to light. Another problem with many of the prior art single-step direct image-forming electrolytic developers has been their inability to produce images having as high a contrast and density as is desired.

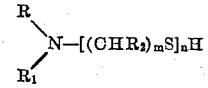
It is, therefore, an object of our invention to provide a novel class of single-solution, one-step electrolytic developers for photoconductographic processing.

Another object is to provide for photoconductographic processing an electrolytic developer that produces images having higher density and higher contrast than those produced from thiosulfate-silver complex, thiourea-silver complex developers or any other one-step developers previously available.

Another object is to provide an electrolytic developer which will not react chemically with the photoconductographic surface after processing, and whose rate of printout in the presence of light is greatly reduced, thus eliminating the necessity for removing the excess unused solution by washing.

Still another object is to provide an electrolytic developer that is valuable for protoconductographic processing to form permanent, dense images that are stable in the presence of heat and light, as well as odorless in the final print. Still other objects will become evident from the following specification and claims.

These and other objects are accomplished by the use of the novel single-step direct image-forming electrolytic developer of our invention. According to our invention, ω-aminoalkanethiol silver ion complexes are valuable developing agents for use in our single-step direct image-forming electrolytic developer for photoconductographic processing. The ω-aminoalkanethiols valuable for making our silver ion complex developing agents may be described but not limited to the compounds of the following formula:



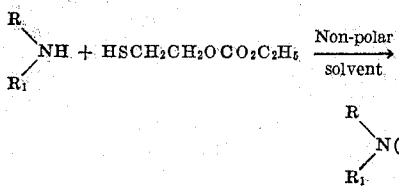
(I)

in which m represents an integer of at least 2 and not more than 4; n represents a number having an average value of from 1 to about 5; R and R_1 each represents a hydrogen atom, an aliphatic group having from 1 to 6 carbon atoms, such as an alkyl group having from 1 to 5 carbon atoms, for example methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, tertiary butyl, amyl, isoamyl, a substituted alkyl group, such as 2-hydroxyethyl, 2-aminoethyl, 2-hydroxypropyl, 3-aminopropyl, 1-methyl-2-hydroxyethyl, 1-methyl-2-aminoethyl, 2-hydroxybutyl, 1,2,3,4,5-penthydroxy-n-hexyl, 3-aminobutyl, 3-hydroxy-1-methylpropyl, 2-amino-1-methylpropyl, methoxyethyl, ethoxyethyl, propoxyethyl, propoxypropyl, etc., an unsaturated alkyl group, such as allyl, butenyl, etc., an alicyclic group, such as cyclohexyl, cyclopentyl, cyclo-

butyl, etc., such that R and R_1 may be the same or different, or R and R_1 together may represent the atoms necessary to complete with the nitrogen atom a heterocyclic group preferably having from 5 to 6 atoms in the ring, such as pyrrolyl, morpholino, piperadino, N-methylpiperazino, piperazino, etc., and where R_2 is hydrogen or hydroxymethyl.

The 3-aminopropanethiols and 4-aminobutanethiols were prepared by methods described in the literature.

The 2-aminoethanethiols are readily prepared from the corresponding amine by a reaction illustrated by the following equation:



In this reaction, ethyl 2-mercaptoethylcarbonate, when added to a refluxing mixture of 2 mole excess amine in a non-polar solvent will give 60% to 96% yields of the related 2-aminoethanethiol in which *n* equals 1. The preparation of ethyl 2-mercaptoethylcarbonate is described in Johnson et al. copending U.S. patent application, Serial No. 80,970, filed January 6, 1961. The other products of the reaction are oligomers, that is, low molecular weight polymers in which *n* equals 1, 2, 3, 4, etc, such that the average value of *n* is from 1 to about 5. We have found that it is unnecessary to separate the products of this reaction, in fact, in some cases, the use of reaction mixtures to make our electrolytic developers actually enhanced the density, the contrast or both density and contrast of the electrolytically formed images. This discovery has made the invention more practical since separation of the oligomeric products is accomplished by fractional distillation, which for the higher boiling amines becomes difficult and expensive. Since the reaction mixture may be utilized according to our invention, we are able to use a much wider group of amine starting materials which would not be isolable by normal procedures. Furthermore, the cost of the silver complex developing agents is reduced because the yield includes all the oligomers and the work-up of the product involves only the removal of solvent and excess amine. Other methods known to the art are equally satisfactory for the preparation of specific compounds.

The following will further illustrate the 2-aminoethanethiols of our invention and their preparation. The 2-aminoethanethiols in Table I which follows were prepared by the addition of ethyl 2-mercaptoethylcarbonate to a refluxing mixture of amine and solvent under an effective condenser, followed by an additional 2 hours of refluxing. Solvent and excess amine were then removed under aspirator vacuum and the product was the material remaining in the flask. The compounds for which *n* is an integer were distilled through a packed column with a variable reflux-ratio head. The value of *n* was determined by iodometric titration and confirmed by elemental analysis. In cases in which *n* is not an integer it represents an average value for a mixture.

TABLE I

No.	R_1	R	Molar Excess Amine	Solvent	*n* or average *n*	Percent Yield
1	$HOCH_2CH_2$—	H—	2	toluene-dioxane	1	64.5
2	$HOCH_2CH_2$—	H—	2	do	2	27.0
3	$HOCH_2CH_2$—	H—	2	do	1.35	86.0
4	$HOCH_2CH_2$—	H—	0	dioxane	1.67	97.5
5	$(CH_3)_3C$—	H—	2	toluene	1	15.0
6	$HOCH_2(CH_3)_2C$—	H—	0	dioxane	2.90	66.5
7	$(HOCH_2)_2(CH_3)C$—	H—	0	do	3.43	87.0
8	$HOCH_2CH_2$—	CH_3—	2	toluene	1	67.0
9	$HOCH_2CH_2$—	CH_3—	2	do	1.41	100.0
10	$CH_3NHCH_2CH(OH)CH_2$—	CH_3—	−0.5	dioxane	1	47.5
11	$HOCH_2CH_2$—	$H_2NCH_2CH_2$—	0	toluene-dioxane	1.30	88.0
12	$HOCH_2CH_2$—	$H_2NCH_2CH_2$—	0	dioxane	1.75	69.8
13	$HOCH_2CH_2$—	$H_2NCH_2CH_2$—	−0.5	toluene-dioxane	1.87	88.2
14	$HOCH_2CH_2$—	$H_2NCH_2CH_2$—	1	toluene	2.42	61.0

The elemental analysis for compound No. 3 in Table I is as follows:

	C	H	N	S
Analysis Calculated	39.4	8.7	9.9	30.4
Analysis Found	39.6	8.8	9.9	29.0

The electrolytic developer in its simplest form consists of a water solution of the ω-aminoalkanethiol-silver ion complex. This is formed by adding, slowly with stirring, distilled water containing a silver compound which furnishes silver ions to a distilled water solution of the ω-aminoalkanethiol or mixture of ω-aminoalkanethiols. Various silver compounds can be used to furnish the silver ions, for example, silver acetate, silver lactate, silver peroxide, the silver halides, and other silver compounds including silver nitrate, which is the preferred compound for this purpose. The pH of the resulting complex is adjusted where necessary by the dropwise addition of a basic material having a low ionic conductivity, such as for example 2-aminoethanol.

We have found that it is advantageous to add magnesium acetate or calcium acetate to the developer solution. In addition to this, acetic acid may also be added. When one of these acetates or the acetate and acetic acid are used, they are generally incorporated with the distilled water solution of the 2-aminoethanethiol used to prepare the developer solution.

The pH of the 2-aminoethanethiol-silver ion complex developer solution either with or without the magnesium acetate addition may be varied over a wide range. A study made of a typical 2-hydroxyethylaminoethanethiol compound showed that the pAg, that is, the logarithm of the reciprocal of the silver ion concentration was found to vary somewhat with variations of pH. Increasing the pH from 4.7 to 6.0 produced a 0.3 log E increase in the toe speed (that is increased the density of the low density portions of the sensitometric curve relating density to log E) and a greater increase in shoulder speed (that is increased the density of the upper portions of the sensitometric curve), an increase in gamma, and an increase in density from 0.46 to 0.80. At pH values between 6 and 7, there was a further (0.3 log E) increase in toe speed, and shoulder speed with a small increase in density. Above a pH of 7 (up to 9.0 or 10.0), there was little change in the image characteristics. The electrolytic developers are at their optimum pH values when adjusted to 7.0. Doubling the concentration of magnesium acetate produced no radical change in these results.

The magnesium acetate and the acetate ions in the solution act as a buffer for the silver ion complexed thioureas and as an antishorting agent. For the silver ion complexed with the 2-aminoethanethiols, the magnesium ace-

tate functions mainly as an antishorting agent at concentrations of from 3% to 5%, since at the operating pH of these developers (pH equals 7), we are above the buffering zone of this buffer which is in the range of pH's of from 5 to 5.5. It has been noticed that with some of these silver-complex developers, the magnesium acetate provides additional stability for the excess developer left on the surface of the photoconductor. This is believed to be due to a shift in equilibrium of the complex in the presence of magnesium acetate, which reduces the zinc oxide catalyzed reduction of silver ions by light.

The pAg of a typical developer made from a 2-hydroxyethylaminoethanethiol compound was varied over a wide range by the addition of silver nitrate to lower the pAg and by the addition of complexing agent to raise it. The pH and the magnesium acetate concentration was held constant. From a pAg of 7.8 (high silver ion concentration) to a pAg of 11.1 (low silver ion) there was no radical changes in developed image characteristics such as density, contrast, and speed but there was some change in image tone, background stability, and shorting. Too low a pAg produced increased shorting of the layer and decreased the stability of the background of the print to light. Too high a pAg produced brown image tones. For optimum results, the pAg should be that produced by the equimolar ratio of silver ions to ligand, that is, the complexing agent.

The concentration of our developers may be varied over wide ranges. For example, it may be varied from 0.05 to 0.2 molar. Very little change occurs in electrolytically developed image density or contrast from doubling the normal concentration. Between ½ and 1 times the normal concentration (0.1 molar) there was a slight loss in density in the shoulder region of the sensitometric curve and a change in tone of the silver deposit in this region. Below ½ the normal concentration, there was a further loss in image density in the regions of higher photocurrents and a "solarization" like effect with a change in image tone from neutral to brown being observed. The toe region of the sensitometric curve remained essentially constant throughout the concentration range from ¼ to 2 times the normal concentration. A good concentration is from 0.05 to 0.2 molar, and there is not much to be gained by increasing the concentration above 0.1 molar in most cases.

The developer solution is applied to the photoconductographic material in any convenient way so that there is a film of the developer solution covering the photoconductor surface to be developed. For example, the developer may be applied with a roller applicator, a sponge, a brush, poured over the photoconductor surface and then distributed by some suitable means, or the photoconductographic element may be immersed in a tray containing the developer solution so that it covers the photoconductive surface. The developer solution may be applied to the photoconductor surface either before or after exposure of the element to the light image. When the developer is applied before exposure, it is possible to perform the electrolysis either during or after exposure. For the electrolytic development, the conducting layer of the photoconductographic element is made the cathode and an anode is then placed in contact with the developer solution so that in those areas where the photoconductor has been exposed to light and is thus made electrically conducting, there is a cathodic deposition of silver from the developer solution. The anode used in this process may take on a wide range of form, for example, it may be a stationary rod, plate, or transparent surface film, or it may be a moving electrode which may or may not be used simultaneously to apply the developer solution, such as a roller, brush, viscose sponge, etc. When a moving electrode is used, electrolysis takes place as the electrode is moved across the photoconductor layer. Since the moving type of electrode electrolyzes only a part of the photoconductor surface at a given time, higher current densities are applied for a given total current than would be possible with a fixed electrode. A wide range of voltages may be used for effecting the electrolytic development, for example, the voltage may range from 30 up to the breakdown potential of the photoconductive layer and yield good results. Voltages from 60 to 80, however, are preferred for typical photoconductographic materials.

Since the photoconductive layers act as rectifiers, alternating current as well as direct current can be used in the practice of our invention. Our invention is not limited to any particular mode of development. Practically all photoconductographic developing systems can be used to advantage with our developers.

The single-step direct image-forming electrolytic developers of our invention and their use are further illustrated by the following specific examples, which are illustrative and are not to be considered as limiting the scope of our invention.

Example 1

The electrolytic developer was prepared as follows:

2.3 g. 2-aminoethanethiol hydrochloride (Evans Chemetics)
10.0 g. magnesium acetate tetrahydrate
1.0 g. acetic acid (glacial)
100 cc. distilled water

to the above solution was added slowly, with stirring, a solution of:

3.4 g. silver nitrate (purest grade)
100 cc. distilled water.

2-aminoethanol was added dropwise to adjust pH to 7.0. The pAg was 10.2.

A sheet of commercially available dye-sensitized zinc oxide in resinous binder coated on an aluminum foil-paper laminate, was exposed for 5 seconds to 400 ft.-c. tungsten illumination through a 0.3 density increment photographic stepwedge. The resulting conducting image was developed electrolytically using the above prepared developer solution contained in a viscose sponge brush electrode held at 60 volts potential, positive with respect to the photoconductive layer, and one-stroke development at a rate of 2 inches per second. A positive stepwedge pattern resulted consisting of reduced silver and perhaps silver sulfide and silveroxide and other dense reaction products whose density for the highest exposure was 0.85 and whose gamma was 0.85.

Example 2

The electrolytic developer was prepared as follows:

1.25 g. 2-(2-mercaptoethylamino)ethanol
5.0 g. magnesium acetate tetrahydrate
50 cc. distilled water

to the above solution was added slowly, with stirring, a solution of:

1.7 g. silver nitrate (purest grade)
50 cc. distilled water.

2-aminoethanol was added dropwise to adjust pH to 7.0. The pAg was 8.5.

The dye-sensitized zinc oxide layer was exposed and developed as in Example 1 using the above prepared developer. A positive step-wedge pattern resulted consisting of reduced silver and silver sulfide whose density for the highest exposure was 0.82 and whose gamma was 1.10.

Similarly, developers were made with oligomeric mixtures in which the average value of n in the silver ion complexing agent varied from 1 to 2.78 and these developers were used in an electrolytic development process as described above. The following Table II summarizes the maximum density, the number of steps, and the gamma or contrast produced in photoconductographic layers developed with these developers.

TABLE II

n avg.	Density	No. Steps	γ
1.00	0.82	6½	1.10
1.35	0.92	7	0.95
1.67	0.85	7½	0.92
1.87	0.90	8½	0.70
2.00	0.85	6½	1.00
2.78	0.80	9	0.64

Example 3

The electrolytic developer was prepared in the following manner:

2.70 g. 2[N-(2-mercaptoethyl)N-methyl] aminoethanol
10.0 g. magnesium acetate tetrahydrate
1.0 cc. acetic acid (glacial)
100 cc. distilled water

to the above solution was added slowly, with stirring, a solution of

3.4 g. silver nitrate (purest grade)
100 cc. distilled water.

2-aminoethanol was added dropwise to adjust pH to 6.5. The pAg was 7.70.

The dye-sensitized zinc oxide layer was exposed and developed as in Example 1 using the above prepared developer. A positive step-wedge image pattern resulted consisting of reduced silver and some silver sulfide whose density for the highest exposure was 0.80 and whose gamma was 1.00.

Similarly, a developer solution was prepared as above in which N-methyl-2-hydroxyethylaminooligoethylene sulfide complexing agents having an average value of 1.41 for *n* was used. A dye-sensitized zinc oxide layer was exposed and developed as in Example 1 but using this developer. The developed image had a density of 0.80 for the highest exposure, and a gamma of 1.18.

Example 4

The electrolytic developer was prepared in the following manner:

7.24 g. 8-mercapto-6-thia-3-azaoctanol
20.0 g. magnesium acetate tetrahydrate
3 cc. acetic acid (glacial)
200 cc. distilled water at 80° C.

added slowly, with stirring, a solution of:

7.10 g. silver nitrate (purest grade)
200 cc. distilled water at 80° C.

The pH was adjusted to 6.0 with 2-aminoethanol. The pAg was 10.5. The developer, was cooled and aged 24 hours, then filtered before use.

Some of the above developer was poured into the electrolytic developer tray of a Model 23 Microfilm Reader-Printer (Minnesota Mining and Manufacturing Company). The zinc oxide paper in the machine was exposed for 10 seconds to 125 ft.-c. through a 1 mm. step-width, 0.3 density increment photographic step-wedge projected 9× enlargement. Development was standard machine development at 80-volts potential, the zinc oxide electrode being the cathode, a silver electrode tray liner the anode for the sponge development. A positive step-wedge image pattern resulted consisting of reduced silver with some silver sulfide whose density for the highest exposure was 0.83 and whose gamma was 0.90. There were six visible density steps above a density of 0.15. As a comparison of this developer with one of those of the prior art, another sheet of the same zinc oxide coating was exposed and developed as above using a commercially available silver nitrate-thiourea complexed developer solution. The resultant step-wedge image had a density of 0.79 for highest exposure and a gamma of only 0.66. There were eight visible density steps above a density of 0.15 with this developer.

Example 5

The electrolytic developer was prepared in the following manner:

2.0 g. N-(2-hydroxyethyl)-2-aminoethylaminooligoethylene sulfide (*n*=1.75)
5.0 g. magnesium acetate tetrahydrate
0.5 cc. acetic acid (glacial)
50 cc. distilled water at 80° C.

to the above solution was added slowly, with stirring, a solution of:

1.7 g. silver nitrate (purest grade)
50 cc. distilled water.

The pH was adjusted to 7.0 with 2-aminoethanol. The pAg was 7.70.

A dye-sensitized zinc oxide layer coated on aluminum foil-paper laminate was exposed and developed as in Example 1 using the above prepared developer solution. The positive step-wedge image pattern consisting of reduced silver and some silver sulfide at the region of highest exposure, had a density of 0.90 and a gamma of 0.78.

Example 6

The electrolytic developer was prepared in the following manner:

7.8 g. 2-hydroxyethylaminooligoethylene sulfide (*n*=1.35)
250 cc. distilled water

added slowly with stirring, a solution of:

8.5 g. silver nitrate (purest grade)
250 cc. distilled water.

Add:

25.0 g. calcium acetate monohydrate.

The pH was adjusted to 6.5 with 2-aminoethanol. The pAg was 11.25.

A dye-sensitized zinc oxide layer coated on aluminum foil-paper laminate was exposed and developed as in Example 1 using the above prepared developer solution. The positive step-wedge image pattern consisting of reduced silver and some silver sulfide had a density of 0.85 and a gamma of 0.90.

Our invention is further illustrated by the accompanying drawings, FIG. I, FIG. II, FIG. III and FIG. IV.

In FIGURE I, light from light source **11** is passed through the processed photographic image **12** to expose the light-sensitive photoconductive layer **13** that is coated on the conductive layer **14** which is on the support **15**.

In FIGURE II, the light exposed image in the left-hand portion of layer **13** has been developed electrolytically by the passage of a direct current through the film **17** of 2-(2-mercapto-ethylamino)ethanol-silver ion complex developer of Example 2 applied by the viscose sponge **16** and between sponge **16** which serves as the anode and the light exposed conducting areas of the photoconductive layer areas which are made the cathode.

FIGURE III shows the completely developed image on layer **13** made by the process illustrated by FIGURE II.

FIGURE IV shows sensitometric curves A and B, relating the density and the logarithm of the exposure producing the density. Curve A was obtained from the print produced in Example 2 using an electrolytic developer containing 2-(2-mercapto-ethylamino)ethanol-silver ion complex. Curve B was obtained from a print made by electrolytically developing another sample of the same photoconductographic material with the same exposure in a commercial prior art developer.

A comparison of curves A and B illustrates the sharper toe, higher contrast and higher shoulder densities that characterize photoconductographic prints developed with our developers from prints developed with a typical prior

art developer. Our print has 40% less density at the 7th step and 21% more density as step 1 than the corresponding print produced with the prior art developer. Curve A has a slope of about 0.78 in its straight line portion compared to a slope of about 0.5 for curve B. Thus the contrast as measured by the slope of these curves is about 56% higher for our prints than for the prior art prints.

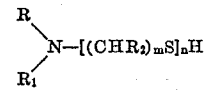
The novel ω-aminoalkanethiol-silver ion complex developers of our invention are valuable for use in electrolytic processing of photoconductographic materials in a single-step direct image-forming process. Typical developing solutions are readily prepared from 2-aminoethanethiols or mixtures of these thiols which are prepared by reacting the appropriate amine with ethyl 2-mercaptoethylcarbonate or by other procedures known to the art. The product of this reaction can be used for preparing the silver complex merely by removal of the solvent and excess amine from the crude product. No further purification is needed unless for some reason it is desired to use a pure 2-aminoethanethiol which can be prepared from the reaction mixture by fractional distillation. The ω-aminoalkanethiol-silver ion complex developers are characterized by having greatly improved stability over prior art developers. For example, these developers can be kept for 6 months and longer without noticeable change in their performance while some prior art developers have a useful storage life of only about one week. The developers are characterized by being relatively odor-free as compared to some prior art developers which have obnoxious odors. Our developers produce images having characteristically a shorter or sharper toe, a higher gamma and a higher density than the prior art developers. Because of the small difference in density between the background and the image areas of most microfilm negatives, it is very difficult to produce a photoconductographic print using developers of the prior art without having produced an undesirable background density on the developed copy. Our developers produce prints with no background, using the poorest negatives we could find. The developed images are stable to both heat and light, and the background areas are not subject to printout as readily as are photoconductographic products developed with prior art developers. Because our developing agents are not as chemically reactive with the photoconductors when they are left on the photoconductor surface after processing even upon exposure to light, it is not necessary to wash the processed photoconductographic material. However for archival quality, washing is required. Magnesium acetate, or calcium acetate although not necessary in our developing solutions, can be used to advantage in improving image quality by reducing any tendency there may be for the photoconductor to short. Our novel developer solutions are particularly valuable, not only for their desirable and valuable characteristics, but because they can be used in a wide variety of commercially available photoconductographic developing systems.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of silver ions complexed with an ω-aminoalkanethiol.

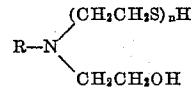
2. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of silver ions complexed with at least one ω-aminoalkanethiol selected from those having the formula:



wherein *m* represents an integer of from 2 to 4; *n* represents a number having an average value from 1 to about 5; R and R_1 each represent a member selected from the class consisting of (1) a hydrogen atom, (2) an aliphatic group having from 1 to 6 carbon atoms, (3) an alicyclic group having from 3 to 6 carbon atoms, and (4) the atoms such that when R and R_1 are connected they form with the nitrogen atom a heterocyclic ring; and R_2 is a member selected from the class consisting of a hydrogen atom and a hydroxymethyl group.

3. An electrolytic developer of claim 2 in which the silver ions are complexed with oligomeric mixtures of 2-aminoethanethiols in which each 2-aminoethanethiol molecule has the same value for R and the same value for R_1 and a different value for the number *n*, such that the average value for *n* for the 2-aminoethanethiol molecules in the mixture is in the range of from more than 1 to not more than 6.

4. A single-step direct image-forming electrolytic developer for photoconductographic processing containing an aqueous solution of silver ions complexed with a 2-aminoethanethiol selected from those having the formula:



wherein R represents a member selected from the class consisting of (1) a hydrogen atom, (2) a lower alkyl group having from 1 to 5 carbon atoms, (3) a hydroxyalkyl group having from 1 to 5 carbon atoms, (4) an aminoalkyl group having from 1 to 5 carbon atoms, (5) an alkoxyalkyl group having from 2 to 6 carbon atoms, (6) an unsaturated alkyl group having from 2 to 5 carbon atoms, (7) and an alicyclic group; *m* represents an integer of from 2 to 4; and *n* is a number having an average value of from 1 to about 5.

5. An electrolytic developer of claim 2 in which the silver ions are complexed with 2-(2-mercaptoethylamino) ethanol.

6. An electrolytic developer of claim 2 in which the silver ions are complexed with 2[N-(2-mercaptoethyl)N-methyl]aminoethanol.

7. An electrolytic developer of claim 2 in which the silver ions are complexed with 2-hydroxyethylaminooligoethylene sulfide having an average *n* value of from 1 to 3.

8. An electrolytic developer of claim 2 in which the silver ions are complexed with N-(2-hydroxyethyl)-2-aminoethylaminooligoethylene sulfide.

9. A single-step direct image-forming electrolytic developer for photoconductographic processing, containing an aqueous solution of (1) silver ions complexed with an ω-aminoalkanethiol and (2) a compound selected from the class consisting of calcium acetate and magnesium acetate.

10. An electrolytic developer of claim 9 in which the ω-aminoalkanethiol is 2-(2-mercaptoethylamino) ethanol.

11. An electrolytic developer of claim 9 in which the ω-aminoalkanethiol is 2[N-(2-mercaptoethyl)N-methyl]-aminoethanol.

12. An electrolytic developer of claim 9 in which the ω-aminoalkanethiol is 2-hydroxyethylaminooligoethylene sulfide having an average *n* value of from 1 to 3.

13. An electrolytic developer of claim 9 in which the ω-aminoalkanethiol is N-(2-hydroxyethyl)-2-aminoethyl-aminooligoethylene sulfide.

14. An electrolytic developer of claim 9 in which the ω-aminoalkanethiol is 2-aminoethanethiol.

15. A single-step process for electrolytically developing photoconductographic material comprising a conducting layer coated with an image exposed photoconducting layer, said electrolytic development comprising the steps of (1) applying an electrolytic developer solution selected from those of claim 1 and (2) passing an electrolyzing current through the said developer between an anode in contact with it and the image exposed areas of said photoconducting layer as the cathode, such that a corresponding silver image is deposited on the surface of said photoconducting layer.

16. A process of claim 15 in which the electrolytic developer solution contains an aqueous solution of calcium acetate and silver ions complexed with an ω-aminoalkanethiol.

No references cited.