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3,384,560 PHOTOCONDUCTIVE DEVELOPING SOLUTIONS CONTAINING QUATERNARY AMMONIUM SALT ANTI-SHORTING AGENTS

Raymond F. Reithel, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
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This invention relates to photoconductography and more particularly to novel electrolytic developing compositions for use in photoconductography.

At the present time, the quality of image reproduction obtained by conventional electrolytic development of image-bearing photoconductive materials has not been satisfactory. Typically, an exposed photoconductive material, such as a paper support coated with particulate zinc oxide in a resin binder, is electrolytically developed using an aqueous developer containing a silver salt. During image development by this method, electrical shorts are prone to occur through the photoconductive material. This electrical shorting through the photoconductive coating produces black spots at the point of the short. It is believed that the spots are formed as the result of the deposition of metallic zinc and silver. The occurrence of these objectional black spots together with the undesirable effect such shorting has on the over-all efficiency of the electrolytic development, severely limits the usefulness of this otherwise desirable method of image reproduction.

There is, therefore, a need for an effective method for reducing the occurrence of electrical shorts during the electrolytic development of image-bearing photoconductive materials. There have been many attempts to obtain a solution to the problem of shorting. Reducing the applied potential during development reduces shorting. This is unsatisfactory because the potential must be reduced to a value too low to be effective for development in order to obtain a high quality developed image. Attempts to reduce shorting by the alteration of the resin binder have also had little success. Magnesium or calcium acetate have been tried as addenda to the developing composition. These materials while not reducing the occurrence of shorting do tend to negate some of its harmful effects. During the development step they precipitate an insoluble electrical insulating hydroxide at the point of the short to inhibit the deposition of free metal. The shorting still occurs, however, and the remedy while reducing the efficiency of the development also tends to block some of the area normally reserved for image development. Both these factors operate to reduce the quality of the resultant image.

One object of the present invention is to provide a novel process for electrolytically developing latent images contained on exposed photoconductive materials.

Another object of the invention is to provide novel electrolytic developing compositions which are capable of effectively reducing the electrical shorting normally encountered in electrolytic development of photoconductive materials.

A further object of the present invention is to provide the above objects without a reduction in the desired density of the resultant developed image.

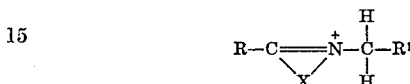
The above and other objects and advantages of the invention are achieved as further described hereinafter by the addition of various quaternary ammonium salts to otherwise conventional electrolytic developer compositions. The inclusion of an effective amount of the quaternary ammonium salts according to this invention into electrolytic developer compositions substantially decreases

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the extent of electrical shorting which is normally prone to occur during the electrolytic development of photoconductive materials which are useful in photoconductographic systems.

In general, the quaternary ammonium salts according to this invention, which have been demonstrated to have the ability to effectively reduce the occurrence of electrical shorting in photoconductographic systems can be characterized as anti-shortening agents of the following types:

(A) those whose cation contains an ammonium nitrogen in a five to six membered heterocyclic nucleus and characterized by the general formula

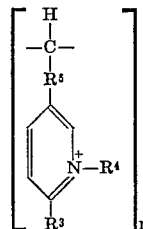


wherein R is a lower alkyl radical, R¹ is either a hydrogen atom or a substituted or unsubstituted lower alkyl radical, and X is an acyl residue which forms a heterocyclic group with the



such as a benzothiazolium, naphthothiazolium, pyridinium, isoquinolinium, quinolinium, 5-vinyl-pyridinium and the like radicals;

(B) those whose cation has the general formula:



wherein n is an integer selected such that in combination with a selected concentration of the resultant compound, it will produce a viscosity having a value in the range of from about 2 to about 10 centipoises at 20° C. in the developer, R³ and R⁴ are substituted or unsubstituted lower alkyl radicals, and R⁵ is a lower alkylene radical. The lower alkyl radicals of the above cations typically contain 1 to 6 carbon atoms such as methyl, ethyl, n-propyl, t-butyl, amyl, n-hexyl, etc. The lower alkylene radical of the above polymeric cation typically has 1 to 4 carbon atoms such as methylene, ethylene, n-propylene, n-butylene, etc.

The anions useful with both of the above types of cations may be selected from among any of the known anions for the compounds of such classes. Typically, an anion of the form R⁶Z may be utilized where Z is an anionic residue and R⁶ is a lower alkyl typically having 1 to 6 carbon atoms or an aryl radical such as phenyl and naphthyl radicals. Anions such as alkylsulfates, aryl sulfonates or the like may advantageously be used.

For the proper functioning of compounds of type (A) above, the cation and anion substituents should be selected such that the resultant compound will be insoluble in a selected developer composition at pH values above about 7. This property is necessary for the prevention of electrical shorting by the formation of an insoluble, substantially colorless, hydrophobic, non-conductive filler that effectively reinforces any area of the photoconductive layer that exhibits dielectric weakness during electrolytic development.

The characteristic action exhibited by type (B) compounds is observed as an increase in the viscosity of the developer electrolyte to which they are added. This prop-

erty appears to slow the penetration of the electrolyte into the photoconductive layer during development thereby substantially preventing the occurrence of electrical shorting.

Individual preferred compounds of types (A) and (B) above include: Type (A)—

2,3-dimethylbenzothiazolium-p-toluenesulfonate;
2,3-dimethyl- β -naphthothiazolium-p-toluenesulfonate;
2,2'-ethylene-bis(N-methylpyridinium-p-toluenesulfonate);
2,3-dimethylisoquinolinium-p-toluenesulfonate; and
1,2-dimethylquinolinium-p-toluenesulfonate;

Type (B)—

poly(1,2-dimethyl-5-vinylpyridinium-p-toluenesulfonate);
and
poly(1,2-dimethyl-5-vinylpyridinium-methosulfonate).

The total quantities of any particular quaternary ammonium salt or mixtures thereof selected for use according to this invention should be empirically determined for each different system of developing solution and photoconductive material. The concentration needed may vary with changes in developer solution composition and/or changes in the formulation of the specific photoconductive coating or layer. The minimum quantity needed generally is that which will produce a visible indication of an effective elimination of shorting. Typically, it is beneficial to use at least about 0.1 percent by weight of the feature quaternary ammonium salt to be effective, although as previously indicated herein, some circumstances permit smaller amounts. A higher amount can be used, so long as it is under the limit of the solubility of the particular quaternary ammonium salt selected for addition to the developer solution. Generally an excess over the quantity actually needed will do no harm. It is preferred to use the anti-shortening agents disclosed herein in concentrations of from about 0.25 to about 2 percent by weight of the total developing composition.

When utilizing the anti-shortening agents described herein, the developed image density can be increased by the addition to the developing composition of certain density-adjusting agents. The following compounds have been demonstrated to be of particular benefit for use as such density-adjusting agents:

- (a) 1,4-bis(pyridinium oxymethyl) benzene bis-(p-toluenesulfonate);
- (b) 2-thiobarbituric acid;
- (c) glutathione; and
- (d) guanidinium p-toluenesulfonate.

The amount or concentration of such density-adjusting agents used in electrolytic developer compositions will vary with the particular conditions encountered such as the formulation of the developer, the composition of the photoconductive film, and the particular quaternary ammonium salt anti-shortening agent used. Thus, at times while an amount under 0.1 percent by weight may be effective, it is advantageous to use a concentration of from about 0.1 to about 2 percent by weight. The optimum amounts may of course be easily determined experimentally under the conditions of intended use.

In the following examples the basic unmodified electrolytic developer solutions and photoconductive elements employed were selected as exemplary because of their present wide use in photoconductographic systems. This selection of materials permits a comparison which clearly illustrates the improvement in conventional photoconductography made possible by this invention.

It should be emphasized that substantially the same improvement can be obtained in any equivalent photoconductographic system. In organic photoconductor compositions containing for example selenium salts or alloys, cadmium salts or alloys, tellurium salts or alloys, and oxides or sulfides of Mg, Ti, Zn, As, Pb, Sn, Sb, and In and combinations of more than one of them whether

sensitized or not may be used in the photoconductive element which is to be electrolytically developed. Likewise, a wide variety of organic photoconductor compositions may also be used in the practice of this invention. Similarly, developing compositions whether containing silver salts or other useful developing agents may be improved by the utilization of the developer additives according to this invention. The following examples are therefore merely representative of a wide variety of photoconductographic applications to which this invention may be applied.

Example 1.—2,3-dimethylbenzothiazolium-p-toluenesulfonate

An electrolytic developer solution was prepared by dissolving 7.28 grams of 2-hydroxyethylaminooctylthiophene sulfide (having an average molecular weight of about 145) in 250 cc. of distilled water, and admixing into that sulfide solution a solution containing 8.5 grams of silver nitrate in 250 cc. of distilled water. The resulting solution was filtered and 5.0 grams of 2,3-dimethylbenzothiazolium-p-toluenesulfonate was dissolved in the filtrate. The finished electrolytic developer solution had a pH of 6.7 and a pAg of 9.3. A conventional photoconductive sheet containing a coating of zinc oxide in a binder material was exposed for 5 seconds to 400 foot candles of tungsten illumination through a 0.3 log E silver density increment step wedge. The exposed paper was then developed electrolytically by making the paper the cathode and using as an anode a viscose sponge brush electrode saturated with the electrolytic developer solution prepared above. One stroke of the brush anode over the coating of the paper cathode at the rate of 2 inches per second under a 60-volt potential was sufficient to develop the image contained in the photoconductive coating.

The anti-shortening agent-containing developer solution of Example 1 (containing 1 percent of its anti-shortening agent) was compared under parallel conditions with a corresponding electrolytic developing solution wherein calcium acetate (at a concentration of 4.1%) was included as the anti-shortening agent. The anti-shortening characteristics of the developer solution of Example 1 herein were markedly superior to those of the solution containing the calcium acetate as the anti-shortening agent. For example, the developer containing the 4.1% concentration of calcium acetate (monohydrate) showed an average of 6 shorts per square inch at voltage potential of 60 volts, and 12 shorts per square inch at 80 volts, thereby averaging 9 shorts per square inch. The developer of Example 1 showed an average of only 2 shorts per square inch at 60 volts, and 5 at 80 volts, or an over-all average of only 3.5 shorts per square inch. That amounts to the occurrence of 61% less shorts utilizing the anti-shortening agent (type A) of Example 1 of the invention than occurred when calcium acetate monohydrate was used as the anti-shortening agent. The shorts, appearing as variously sized discrete black spots of zinc from the ZnO and deposited silver from the AgNO₃ of the developer were counted by using a 10X magnification binocular microscope.

Example 2

The procedure of Example 1 was repeated four times by replacing the 2,3-dimethylbenzothiazolium-p-toluenesulfonate in each successive formulation with 5 grams of a different one of the following compounds:

- (a) 2,3 - dimethyl - β - naphthothiazolium - p - toluenesulfonate;
- (b) 2,2' - ethylene - bis - (N-methylpyridinium-p-toluenesulfonate);
- (c) 1,2-dimethyl-quinolinium-p-toluenesulfonate; and
- (d) 2,3-dimethyl-isoquinolinium-p-toluenesulfonate.

Each of the developer solutions so modified was employed as an electrolytic developer under the same con-

ditions as Example 1 with substantially the same relative improvement in the prevention of electrical shorting being observed in each case.

Example 3.—Poly-(1,2-dimethyl-5-vinyl-pyridinium-methosulfate)

An electrolytic developer solution was prepared by dissolving 7.28 grams of 2-hydroxyethylaminooligoethylene sulfide (having an average molecular weight of about 145) in 250 cc. of distilled water, and subsequently, admixing into that solution a solution of 8.5 grams of silver

and contains a qualitative comparison of the size of the specks which developed from the shorting in each case. In the preferred embodiment of this invention care should be taken to use developer materials which are substantially free of alkali metal ions. The table shows how a small concentration of one of such ion containing compounds (KNO_3) detrimentally affects electrolytic development. The use of the addendum of this invention is therefore advantageous in decreasing this kind of contamination when compared to the likelihood of such contamination when magnesium and calcium salts are used.

EFFECT OF VARIOUS ANTI-SHORTING AGENTS

| Addendum to Electrolytic Developer | Percent Concentration of Addendum in Developer | Voltage | Average Shorts per inch ² | Size of Shorts | Developer | |
|---|--|-----------------------------|--------------------------------------|----------------|-----------------------|-------------------|
| | | | | | Resistivity (ohm-cm.) | Viscosity, (cps.) |
| Blank..... | | 60 80 60 80 100 | 10 19 12 29 91 | Large..... | 197 | 3.3 |
| Mg(OAc) ₂ ·4H ₂ O, 5%..... | 5 | 60 80 100 | 6 6 6 | | | |
| Ca(OAc) ₂ ·II ₂ O..... | 4.1 | 60 80 100 | 12 57 57 | Small..... | 47 | 3.5 |
| 1, 2-dimethylbenzothiazolium, p.t.s. 1%..... | 1 | 60 80 100 | 2 5 5 | | | |
| Poly-1, 2-dimethyl-5-vinyl-pyridinium, p.t.s. 0.5%..... | 0.5 | 60 80 100 | 1 3 8 | do..... | 50 | 3.5 |
| 0.05%, KNO_3 | 0.05 | 60 80 | 35 52 | | | |
| | | | | Large..... | 195 | 5.3 |
| | | | | | 177 | 3.3 |

nitrate in 250 cc. of distilled water. The resulting solution was filtered, and 2.5 grams of poly-(1,2-dimethyl-5-vinyl-pyridinium-methosulfate) was dissolved in the filtrate. The finished electrolytic developer solution had a pH of 6.7 and a pAg of 9.2. A sheet of photoconductive zinc-oxide-resin coated paper was exposed for 5 seconds to 400 foot candles of tungsten illumination through a 0.3 log *E* silver density increment step wedge. The exposed paper was then developed electrolytically by making the paper the cathode and using as an anode a viscose sponge brush electrode saturated with the electrolytic developer solution prepared above. One stroke of the brush anode over the paper cathode at the rate of 2 inches per second under a 60 volt potential was sufficient to develop the image contained in the coating of the exposed paper.

Example 4.—Poly-(1,2-dimethyl-5-vinyl-pyridinium-p-toluenesulfonate)

An anti-shortening agent electrolytic developer solution was prepared by the method of Example 3 by replacing the poly-(1,2-dimethyl - 5 - vinyl-pyridinium methosulfonate) with 2.5 grams of poly-(1,2-dimethyl-5-vinyl-pyridinium-p-toluenesulfonate). The resulting anti-shortening agent-containing developer solution also showed a pH of 6.7. The resistivity of the solution was 195 ohm-centimeters, and the solution had a viscosity of 5.3 centipoises. It was then used in the same manner, as in Example 3, to saturate a viscose sponge brush anode electrode to develop an exposed zinc oxide-resin coated paper. The developer solution was also compared with an electrolytic developer solution wherein a 4.1% concentration of calcium acetate (monohydrate) was used instead of the present anti-shortening agent. That developer solution showed an average of 25 shorts per square inch (6 shorts at 60 volts, 12 shorts at 80 volts, and 57 shorts at 100 volts). The developer with the present anti-shortening addenda produced only 2 shorts at 60 volts, 3 at 80 volts, 8 at 100 volts, or a total average of 4 shorts per square inch. These comparisons clearly show that in the present developer solution containing a (type B) anti-shortening agent there were about 84% less shorts than were experienced with a similarly prepared developer solution containing calcium acetate monohydrate as an anti-shortening agent.

The following table summarizes the above comparisons

The anti-shortening characteristics of the developer solutions of this invention are thus markedly superior to those of the developer solution containing calcium acetate monohydrate as an anti-shortening agent. It should be considered, however, that the maximum density of prints developed with the anti-shortening developer solution of Example 2 was slightly lower than that of prints developed with the calcium acetate type of anti-shortening developer solution. The observed discrepancy in density can easily be avoided in the practice of this invention while retaining the superior anti-shortening behavior of the developer solution. The slightly lower shoulder density manifested, i.e., in the regions of higher current density, is overcome by adding to the developer solution an amount of another substance effective to adjust the density without adversely affecting the anti-shortening activity.

Such modified embodiment of the invention is illustrated by, but not limited to, the following:

Example 5.—Type B developer with density-adjusting agent

The procedure of Example 3 was repeated with the addition of 5 grams of 2-thiobarbituric acid to the developer solution as a density-adjusting agent. This modified developer when used to develop a zinc oxide image as in Example 3, increased the plating efficiency of that developer and therefore retained the requisite image density particularly in its higher current density regions.

Example 6.—Type B developer solution with glutathione

The procedure of Example 5 was repeated except that 5 grams of glutathione was added to the developer solution in place of 2-thiobarbituric acid. This developer composition was used in the same manner as described for Example 1 to develop sheets of exposed photoconductive zinc oxide-resin coated paper. The behavior of the developer solutions of Examples 5 and 6 were compared with a developer containing calcium acetate (monohydrate) as an anti-shortening agent. The resulting density on the prints developed with the developer solution of these Examples 5 and 6 was the same as shown by the prints developed with the calcium acetate-containing developer while exhibiting the superior resistance to shorting already described. The prints obtained by use of the de-

velopers of Examples 5 and 6 showed an average of only one short per square inch.

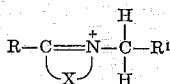
The 2-thiobarbituric acid of Example 5 similarly can be replaced by the same weight of 1,4-bis-(pyridinium-oxymethyl)-benzene bis-(p-toluenesulfonate), and likewise of guanidinium p-toluenesulfonate, to provide additional electrolytic developer solutions containing an effective density-adjusting agent.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

What is claimed is:

1. An aqueous developing composition for electrolytically developing an exposed photoconductive element comprising a quaternary ammonium salt present in an electrolytic developing solution in an amount effective to prevent electrical shorting through a photoconductive element during electrolytic development, the cation of which salt is selected from the group consisting of:

(A) cations having the formula:

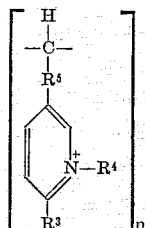


wherein R is a lower alkyl radical, R¹ is selected from the group consisting of a hydrogen atom and a lower alkyl radical, and X is an acyl residue which completes a heterocyclic cationic group with the



and is selected from the group consisting of acyl residues and arylacyl residues; and

(B) polymeric cations having the formula:

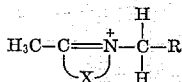


wherein n is an integer, R³ and R⁴ are each a lower alkyl radical, R⁵ is a lower alkylene radical.

2. The aqueous electrolytic developing composition as described in claim 1 containing an image density adjusting agent, which is selected from the group consisting of 1,4-bis-(pyridinium oxymethyl)-benzene bis-(p-toluenesulfonate), 2-thiobarbituric acid, glutathione and guanidinium p-toluenesulfonate, in an amount to be effective to maintain the density of a developed image on a photoconductive element.

3. In an aqueous electrolytic silver ion-containing developing composition for an exposed photoconductive element, the improvement wherein said solution contains dissolved therein an anti-shortening agent which is a member of the class of compounds consisting of:

(A) those wherein the cation contains ammonium nitrogen in a five to six membered heterocyclic nucleus having the structural formula



wherein R is selected from a hydrogen atom and an N-methyl pyridinomethyl radical, and X is a residue which with said group



to which it is linked completes a heterocyclic cationic

group which is selected from the group consisting of benzothiazolium, naphthothiazolium, pyridinium, isoquinolinium, quinolinium and 5-vinyl-pyridinium radicals; the anion of which salt forms a compound insoluble in alkaline aqueous media;

(B) poly-(1,2-dimethyl-5-vinyl-pyridinium p-toluenesulfonate); and

(C) poly-(1,2-dimethyl-5-vinyl-pyridinium methosulfate).

4. An aqueous electrolytic developing composition as described in claim 3 wherein the quaternary ammonium salt is 2,3-dimethylbenzothiazolium-p-toluenesulfonate.

5. An aqueous electrolytic developing composition as described in claim 3 wherein the quaternary ammonium salt is 2,3-dimethyl-beta-naphthothiazolium-p-toluenesulfonate.

6. An aqueous electrolytic developing composition as described in claim 3 wherein the quaternary ammonium salt is 2,2'-ethylene-bis-(N-methylpyridinium-p-toluenesulfonate).

7. An aqueous electrolytic developing composition as described in claim 3 wherein the quaternary ammonium salt is 1,2-dimethylquinolinium-p-toluenesulfonate.

8. An aqueous electrolytic developing composition as described in claim 3 wherein the quaternary ammonium salt is 2,3-dimethyl-isoquinolinium-p-toluenesulfonate.

9. An aqueous electrolytic developer composition as described in claim 3 containing a density-adjusting agent selected from the group consisting of:

(a) 1,4-bis-(pyridinium oxymethyl)-benzene bis-(p-toluenesulfonate),

(b) 2-thiobarbituric acid,

(c) glutathione, and

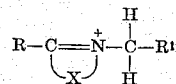
(d) guanidinium p-toluenesulfonate

in an amount to be effective in preventing a reduction in the observed density of an image contained in a developed photoconductive element.

10. An aqueous electrolytic developer composition as described in claim 9 wherein the density-adjusting is present in the range of from about 0.1 to about 2 percent by weight.

11. In a method of electrolytically developing an exposed photoconductive element by the application of a potential between two electrodes through an electrolyte where the electrolyte is in contact with the photoconductive element and the element is one electrode, the improvement comprising substantially reducing the extent of electrical shorting through the exposed surface of the element during such development by the addition to the developer electrolyte of an effective amount of a compound selected from the group consisting of compounds:

(A) whose cation is selected from cations having the formula



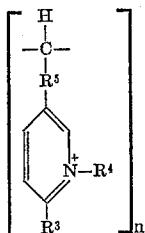
where R is a lower alkyl group, R¹ is selected from the group consisting of a hydrogen atom and a lower alkyl group, and X is an acyl residue which completes a heterocyclic cationic group with the



and is selected from the group consisting of acyl residues and arylacyl residues; and whose anion is selected from anions which with the cations will form compounds which are insoluble in water at pH values more alkaline than about 7; and

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(B) whose cation is selected from cations having the formula:



wherein n is an integer, R^3 and R^4 are each lower alkyl radicals, R^5 is a lower alkylene radical, and whose anion has the formula R^6Y wherein R^6 is selected from the group consisting of lower alkyl and aryl moieties and Y is an anionic residue.

12. The method according to claim 11 wherein the electrolytic developing composition contains at least one

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density-adjusting agent selected from the group consisting of

- (a) 1,4-bis-(pyridinium oxymethyl)-benzene bis - (p-toluenesulfonate),
 - (b) 2-thiobarbituric acid,
 - (c) glutathione, and
 - (d) guanidinium p-toluenesulfonate
- in an amount effective to prevent a reduction in the density of the developed image on the photoconductive element.

References Cited

UNITED STATES PATENTS

| | | | |
|-----------|---------|----------------|--------|
| 3,010,883 | 11/1961 | Johnson et al. | 204—18 |
| 3,178,362 | 4/1965 | Sagura et al. | 204—18 |

JOHN H. MACK, *Primary Examiner*.

T. TUFARIELLO, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,384,560

May 21, 1968

Raymond F. Reithel

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 61, after "anti-shortening" insert -- effective concentration of a quaternary ammonium salt anti-shortening --.

Signed and sealed this 14th day of October 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents