

[54] **PHOTOGRAPHIC PHOTOCONDUCTOR SYSTEMS UTILIZING REVERSIBLE REDOX MATERIALS TO IMPROVE LATENT IMAGE LIFE**

[72] Inventors: **Richard F. Bartlett**, Burlington, Mass.;
Itek Corporation, Lexington, Mass.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 510,977, Dec. 1, 1965, abandoned.

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[58] Field of Search **96/1.5-1.8, 27, 96/88-90, 48 PD; 252/501**

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Primary Examiner—Charles E. Van Horn
Attorney—Homer O. Blair, Robert L. Nathans and W. Gary Goodson

[57] **ABSTRACT**

A copy medium comprising a support, a photoconductor, and a reversible oxidizing agent is exposed to produce a latent image of improved stability and then, after a time period of at least 30 seconds, contacted with image-forming materials to produce an irreversible image. Optionally, the reversible oxidizing agent may be applied to the copy medium immediately after exposure. An acidified copy medium is especially preferred since the stability of the latent image is much improved.

26 Claims, No Drawings

PHOTOGRAPHIC PHOTOCONDUCTOR SYSTEMS UTILIZING REVERSIBLE REDOX MATERIALS TO IMPROVE LATENT IMAGE LIFE

This application is a continuation-in-part of copending application U.S. Ser. No. 510,977 filed Dec. 1, 1965, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a photographic process and copy medium utilizing a photoconductor as the photosensitive material.

2. Description of the Prior Art

Photographic systems based on a photoconductor as the photosensitive material are well-known in the art as shown by U.S. Pat. Nos. 3,010,883 and 3,152,903 and British Pat. No. 1,043,250. In these systems a copy medium comprising a photoconductor is exposed to activating radiation to thereby activate the photoconductor in exposed portions and contacting the copy medium either prior or subsequent to exposure to produce a visible permanent image. One of the problems with these photographic-photoconductor systems is that when the copy medium is contacted with image-forming materials such as metal ions prior to exposure and allowed to remain for a substantial period of time in contact with the photoconductor then a reaction occurs between the photoconductor and the image-forming materials known as a "dark reaction." This occurs even though the photoconductor has not been activated as, for example, by exposure to light. This reaction between the photoconductor and image-forming materials shows up in the final developed print as undesirable background fog. By contacting the copy medium with image-forming materials after exposure this fogging problem is overcome. However, the latent image produced by exposure of the photoconductor is reversible and of limited life. This reversible latent image provides a number of advantages such as being able to erase undesired latent images and reuse the copy medium. However, the reversibility feature can provide serious problems also. With proper photoconductor, developer, binder system and other conditions it is possible to develop a visible image from a reversible latent image produced by exposure of the photoconductor containing copy medium for up to a few days. On the other hand, when the conditions are not just right the latent image may have no life or the life of only a few seconds. Thinness of photoconductor layer, conductivity of the support, amount and type of binder and other like factors affect the stability of the latent image. For example, in the production of a metal printing plate a copy medium comprising a metal support having a very thin coating of a photoconductor such as less than about 0.001 centimeter in thickness is exposed imagewise and contacted with a metal ion containing solution to produce a printing plate having a metallic image. After about 30 seconds the latent image in this system has decayed to such an extent that any image produced by reaction with image-forming materials is unsatisfactory for printing under ordinary conditions. After two minutes the latent image has decayed to such an extent that ordinary processing with image-forming materials will not produce any detectable visible image. This latent image decay problem is especially critical where the printing plates to be produced are to be used for color work since any variation in density in any one of the separation plates will throw off the color balance in the final color print.

Numerous attempts have been made to solve this latent image decay problem. However, up to the date of this invention none of these attempts have proven to be satisfactory.

SUMMARY OF THE INVENTION

A copy medium comprising a photoconductor is exposed, contacted with a reversible oxidizing agent to produce a latent image of improved stability and then after a time interval of at least about 30 seconds contacted with image-forming materi-

als to produce an irreversible image. This latent image of improved stability is produced by the reduction of the reversible oxidizing agent by the activated photoconductor. Therefore, the exposed areas of the copy medium now contain a "reversible reducing agent" and the unexposed portions of the copy medium contain the reversible oxidizing agent. An acidic copy medium is preferred because of improved latent image stability. Latent image stability includes length of latent image life and/or the lack of decay of that latent image, i.e., the ability of a latent image to be developed to a given optical density using the same developer system but varying the time intervals between exposure and development. A preferred copy medium has a pH of less than 5 and even more preferably less than 3.

PREFERRED EMBODIMENT(S)

The media of this invention comprise: (1) an image-forming system wherein a photoconductor and a "reversible redox system" are the essential ingredients and (2) a support. The "reversible redox system" is present at the time of activation of the photoconductor as a "reversible oxidizing agent" and is then converted to a "reversible reducing agent" by reaction with the activated photoconductor. In a preferred embodiment the reversible reducing agent latent image thus formed is contacted with a metal ion. The metal ion is reduced to thereby form a metal image corresponding with this latent image pattern. The reversible reducing agent latent image is more stable than the latent image formed solely by exposing a photoconductor to activating radiation. However, this reversible reducing agent latent image can be stabilized even more by acidifying the image-forming system of the copy medium. Also, when the pH of the system is lowered, the redox materials become much better oxidizing agents and are, therefore, more easily reduced by the activated photoconductor. The pH is preferably less than 5 and more preferably less than 3.

The "reversible oxidizing agent" useful in this invention is an oxidizing agent which has a redox potential which enables it to be reduced by an activated photoconductor to form a reversible reducing agent which is more stable than the activated photoconductor produced by exposure of the photoconductor. When a copy medium comprising a photoconductor and a reversible oxidizing agent is exposed to activating radiation a latent image of selective reactivity is produced. This latent image may be visible or invisible. By contacting the copy medium with an image-forming material which will be reduced by the reversible reducing agent of the exposed areas a permanent, irreversible image can be produced.

A preferred class of reversible oxidizing agents are ones having a redox potential E_0 as defined on page 527 of the W. M. Clark, Oxidation-Reduction Potentials of Organic Systems, 1960, of greater than 0.1 and preferably having a value between 0.1 and 0.7. The E_0 of a compound can be varied by adjusting the pH and other factors known to the art to make these compounds suitable for this invention. The practical upper limit for the redox potential is that value at which excessive background fogging occurs on contacting with image-forming materials to produce a permanent image. Preferred materials are organic compounds such as the quinones and especially the aryl quinones including, for example, the benzoquinones and naphthoquinones. Especially preferred are the organic dyes such as the thiazines such as Thionine, Methylene Blue zinc chloride double salt, New Methylene Blue N and Toluidine Blue O; the indophenols such as m-Carboxy-phenol-endo-2,6-dibromo-phenyl, m-Cresol indophenol sodium salt, 1-Naphthol-2-sodium sulphonate-indophenol sodium, and Carvacrol indophenol sodium; the aminoindephenols; azine dyes such as Pinacryptol Green, Phenosafranine and Neutral Red; Quinoneanils and Indoanilines; and oxazines such as Gallocyanine, Indigo Carmine, Phenoxazine, and Phenonaphthoxazine. An especially preferred class of reversible oxidizing agents are the arylamine

dyes and more especially the thiazine dyes such as Thionine or Toluidine Blue.

The photoconductor or photocatalyst preferred in this invention are metal containing photoconductors. A preferred group of such photosensitive materials are the inorganic materials such as compounds of a metal and a nonmetallic element of Group VIA of the periodic table such as oxides, such as zinc oxide, titanium dioxide (TiO_2), zirconium dioxide, germanium dioxide, indium trioxide; metal sulfides such as cadmium sulfide, zinc sulfide and tin disulfide; metal selenides such as cadmium selenide. Metal oxides are especially preferred photoconductors of this group. TiO_2 is a preferred metal oxide because of its unexpectedly good results. TiO_2 having an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature exceeding about 200°C . is especially preferred, and more especially that TiO_2 produced by high temperature pyrolysis of titanium halide.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide, and zinc activated zinc oxide.

While the exact mechanism by which the photoconductors of this invention work is not known, it is believed that exposure of photoconductors or photocatalysts of this invention to activating means causes an electron or electrons to be transferred from the valence band of the photoconductor or photocatalyst to the conductance band of the same or at least to some similar excited state whereby the electron is loosely held, thereby changing the photoconductor from an inactive form to an active form. If the active form of the photoconductor or photocatalyst is in the presence of an electron accepting compound a transfer of electrons will take place between the photoconductor and the electron accepting compound, thereby reducing the electron accepting compound. Therefore, a simple test which may be used to determine whether or not materials have a photoconductor or photocatalytic effect is to mix the material in question with an aqueous solution of silver nitrate. Little, if any, reaction should take place in the absence of light. The mixture is then subjected to light. At the same time a control sample of an aqueous solution of silver nitrate alone is subjected to light, such as ultraviolet light. If the mixture darkens faster than the silver nitrate alone, that material is a photoconductor or photocatalyst.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions. The more energy needed, the higher the frequency to which the photoconductor will respond. It is known to the art that it is possible to reduce the band-gap for these compounds by adding a foreign compound as an activator which either by virtue of its atomic dimensions or by possessing a particular electronic forbidden zone structure or through the presence of traps as donor levels in the intermediate zone between the valence and the conduction band stresses the electronic configuration of the photoconductive compound, thereby reducing its band-gap and thus increasing its ability to release electrons to its conduction band. Phosphors almost necessarily imply the presence of such activating substances. The effect of such impurities may be such as to confer photoconductivity upon a compound which intrinsically is non-photoconductive. On the other hand, excessive impurity content can interfere with a compound acting as a photoconductor as above described.

The photoconductors of this invention may be sensitized to visible and other wavelengths of light by foreign ion doping, addition of fluorescent materials, and/or by means of sensitizing dyes. Bleachable dyes useful for sensitizing the photoconductors of this invention include, for example, the cyanine dyes, the dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes. Additional dyes which are useful for sensitizing the photosensitive medium of this invention are the cyanine dyes described on pages 371-429 in "The Theory of Photographic Process" by C. E. Kenneth Mees published by

McMillan Company in 1952. Other useful dyes include those known to the art as triphenylmethane dyes such as crystal violet and basic Fuchsin, diphenylmethane dyes such as Auramine O, and Xanthene dyes such as Rhodamine B.

Irradiation sources which are useful in this invention for producing the initial latent image include any of the usual irradiation means commonly used with the selected photosensitive material. Thus actinic light, X-rays or gamma rays are effective when photoconductors are used. Beams of electrons and other like particles may also be used in place of the ordinary forms of electromagnetic radiation for forming an image. These various activating means are designated by the term "activating radiation."

In general, the media of the present invention can comprise any suitable support, for example, paper, plastics, wood, and the like, although the preferred supports are metal supports. The non-metal supports may be comprised of any suitable plastic material, which preferably include cellulose acetate and polyesters, particularly polyethylene terephthalate. The support can be in any form such as, for example, sheets, ribbons, rolls and the like. Of course, the support should be of sufficient strength and durability to satisfactorily serve as a photographic or reproduction carrier. When the support comprises a plastic, particularly a polyester, e.g., polyethylene terephthalate, it is advantageous to utilize subbing materials to ensure adhesion of the photosensitive layer to the support, as described hereinbefore.

For the preferred supports, any suitable metallic or substantially metallic backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier can be employed. The support may be in any form such as, for example, sheets, ribbons, rolls, etc. This sheet may be made of any suitable metal or their alloys, as for example the hydrophilic metals such as chromium, nickel, lead, stainless steel, magnesium, or aluminum; or the oleophilic metals such as copper or zinc. Aluminum is preferred because of its desirable physical and chemical properties, as well as its economy. An anodized, grained surface is especially preferred for the aluminum support. The anodized surface may be porous or non-porous. It is important that sufficient insulation be present between the reversible redox system and the metal support in order to prevent chemical reaction. This insulation can be provided by anodization, silicate layers, binder layers or other art recognized methods.

It may be desirable to use a binder agent to bind the photoconductor to the base sheet to aid in improved physical development, or to use a separate insulating layer. In general, these binders are translucent or transparent so as not to interfere with transmission of light therethrough. They are desirably also solvent permeable in order to allow rapid physical development to take place. Preferred binder materials are organic materials such as natural or synthetic polymers. Examples of suitable synthetic polymers are butadiene-styrene copolymer, poly (alkyl acrylates) such as poly (methyl methacrylate) polyamides, polyvinyl acetate, polyvinyl alcohol and polyvinylpyrrolidone. Natural polymers such as gelatin are also useful. Most preferred are those binders which are solvent soluble enough to be readily washed off after development of the image has taken place.

The photoconductor should be conditioned for exposure by storage in the dark from one to twenty-four hours prior to use, heating or other conditioning means known to the art. After conditioning, the photoconductor is not exposed to activating radiation prior to its exposure to activating radiation for recording an image pattern.

The period of exposure to form the latent image will depend upon the intensity of the light source, particular photoconductor, the type and amount of catalyst, if any, and like factors known to the art. In general, however, the exposure may vary from about 0.001 seconds to several minutes.

The reversible latent image pattern of reversible reducing agent stored in media of this invention is most readily converted to an irreversible form by contacting said media with

image-forming materials capable of reacting on contact with the reversible reducing agent of the media to deposit thereon chemical substances so that said pattern can be interpreted either directly or subsequently by visual readout. Suitable image-forming materials include redox systems such as dyes, resins, or physical developers. The most preferred redox systems are physical developers, comprising metal compounds which can react with the reversible reducing agent to precipitate or otherwise deposit thereon reduced species of said compounds.

Physical developers according to this invention are intended to include those image-forming systems such as described in U.S. Pat. Nos. 3,152,903 and 3,390,988, and in British Pat. Nos. 1,043,250 and 1,064,725, each incorporated herein by reference. These image-forming materials include preferably an oxidizing agent and a reducing agent. Such image-forming materials are also often referred to in the art as electroless plating baths. Electrolytic development such as taught in U.S. Pat. No. 3,152,969 can also be used. The oxidizing agent is generally the image-forming component of the image-forming material. However, this is not necessarily true. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. The oxidizing and reducing agent may be combined in a single processing bath, may be in a separate bath, or a separate nucleation bath may precede the physical development. Also one or both of the oxidizing and reducing-agent components may be incorporated in the imaging medium prior to exposure. Preferred oxidizing agents comprise the reducible metal ions having at least the oxidizing power of cupric ion and include such metal ions as Ag^+ , Hg^{+2} , Pb^{+4} , Au^{+1} , Au^{+3} , Pt^{+2} , Pt^{+4} , Ni^{+2} , Sn^{+2} , Pb^{+2} , Cu^{+1} , and Cu^{+2} .

The reducing agent component of the image-forming materials of this invention are inorganic compounds such as the oxalates, formates, and ethylenediaminetetraacetate complexes of metals having variable valence; and organic compounds such as dihydroxybenzenes, aminophenols, and aminoanilines. Also, polyvinylpyrrolidone, hydrazine, and ascorbic acid may be used as reducing agents in this invention. Suitable specific reducing compounds include hydroquinone or derivatives thereof, o- and p-aminophenol, p-methylaminophenol sulfate, p-hydroxyphenyl glycine, o- and p-phenylenediamine, 1-phenyl-3-pyrazolidone, alkali and alkaline earth metal oxalates and formates.

Liquid physical developer systems are preferred for use as image-forming materials because of the excellent results obtained therewith. Any suitable solvent may be utilized. However, aqueous processing baths are preferred. While the pH of the developer is not critical, it has been found the best results are obtained with an acid developer, and especially one having a pH of between about 2 and 5, and especially with organic acids such as citric, gluconic, maleic, and oxalic which are metal complexing agents. A pH of about 2 to 3 is especially preferred.

Additionally, the image-forming materials or physical developers may contain organic acids or alkali metal salts thereof, which can react with metal ions to form complex metal anions. Further, the developers may contain other complexing agents and the like to improve image formation and other properties found to be desirable in this art.

Additional developer systems useful in this invention are those disclosed in the following U.S. Pat. applications filed July 11, 1968: Ser. No. 743,981, entitled "Electroless Copper Plating Baths, Process, and Related Materials;" Ser. No. 743,982, entitled "Photographic Tin Amplification Process and Product;" Ser. No. 743,983, entitled "Improved Physical Development Systems, Processes, and Related Materials;" each of which is incorporated herein by reference.

A copy medium wherein the image-forming materials for producing an irreversible image are applied prior to exposure in such a way as to be separated from reacting with the photoconductor and reversible oxidizing agent, e.g., as by putting them in separate layers is one embodiment of this in-

vention. Development of an irreversible image may be performed after exposure by moistening the copy medium or by other means known to the art.

The physical developers of this invention should be applied for a length of time sufficient to obtain an image of the desired properties. When the copy medium is to be a printing plate the image should be adherently and, in metal base media preferably conductively, bound to the metallic support. This time period will vary according to the thickness of the photoconductor layer or thickness of the insulating layer or other separation layers, the length of exposure, nature of the binder or insulator material, ratio of photosensitive material to binder, and like factors known to the art.

A useful plating bath for amplifying a metallic image which is conductively bonded to a metal support is the one comprising a metal ion and a pickling agent for the metal of the metallic support, e.g., a solution of copper ethylenediaminetetraacetic acid (CuEDTA) and sodium EDTA.

The invention above described is exemplified as follows:

EXAMPLE 1

Sixteen parts by weight of a finely divided titanium dioxide having an average particle size of about 0.03 micron and an initial surface area of about 40 square meters per gram were dispersed in about 75 parts by weight of water in which 0.32 part by weight of sodium hexametaphosphate had been added as a dispersing agent. The pigment was added with stirring, and the mixture was thoroughly agitated to disperse the titanium dioxide uniformly therethrough.

About 4 grams of polyvinyl acetate binder were next combined with the dispersion containing the particulate titanium dioxide. The mixture, which was thoroughly stirred, was then applied to a pellucid substrate. The coating thickness was about 3.5×10^{-4} cm.

The medium was then exposed through a transparency comprising an image pattern to a tungsten filament lamp for about 15 seconds.

The exposed medium was maintained in the dark for about 7 1/2 hours, and then immersed in a saturated methanolic solution of silver nitrate and subsequently in an amplification solution comprising about 30 grams of phenidone and 30 grams of citric acid in about 1 liter of methanol.

A faint image pattern was discernible in the developed medium but the overall photographic quality was undesirable.

EXAMPLE 2

Substantially the same procedure of Example 1 was followed, but prior to exposure a medium similar to that of Example 1 was immersed in a methanolic solution comprising about 5 milligrams of Methylene Blue per 100 milliliters. After exposure the medium was maintained in the dark for 7 1/2 hours and then developed in accordance with the procedure of Example 1. A quality image pattern was obtained in the medium.

Examples 1 and 2 dramatically illustrate the improvements to be obtained in accordance with the practice of this invention. It is to be understood that substantially the same improvements can be obtained when other photoconductor materials such as zinc oxide and the like are included in media of this invention.

EXAMPLE 3

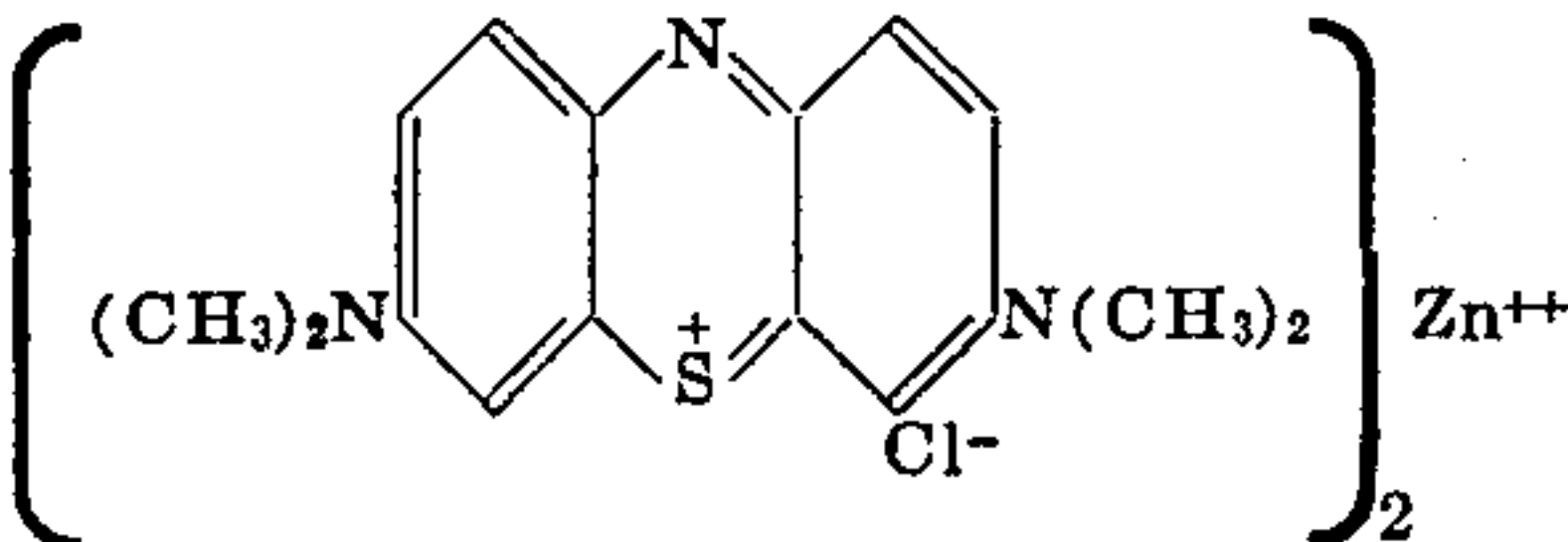
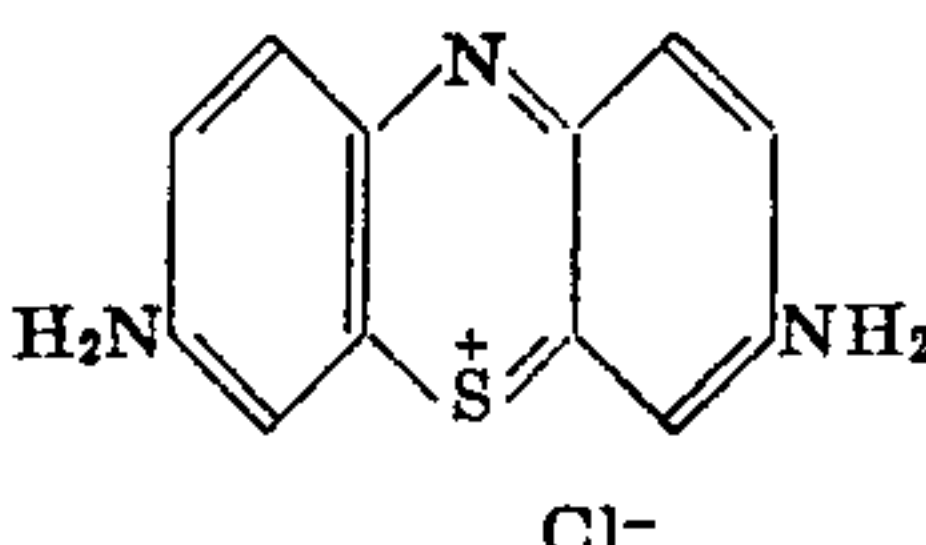
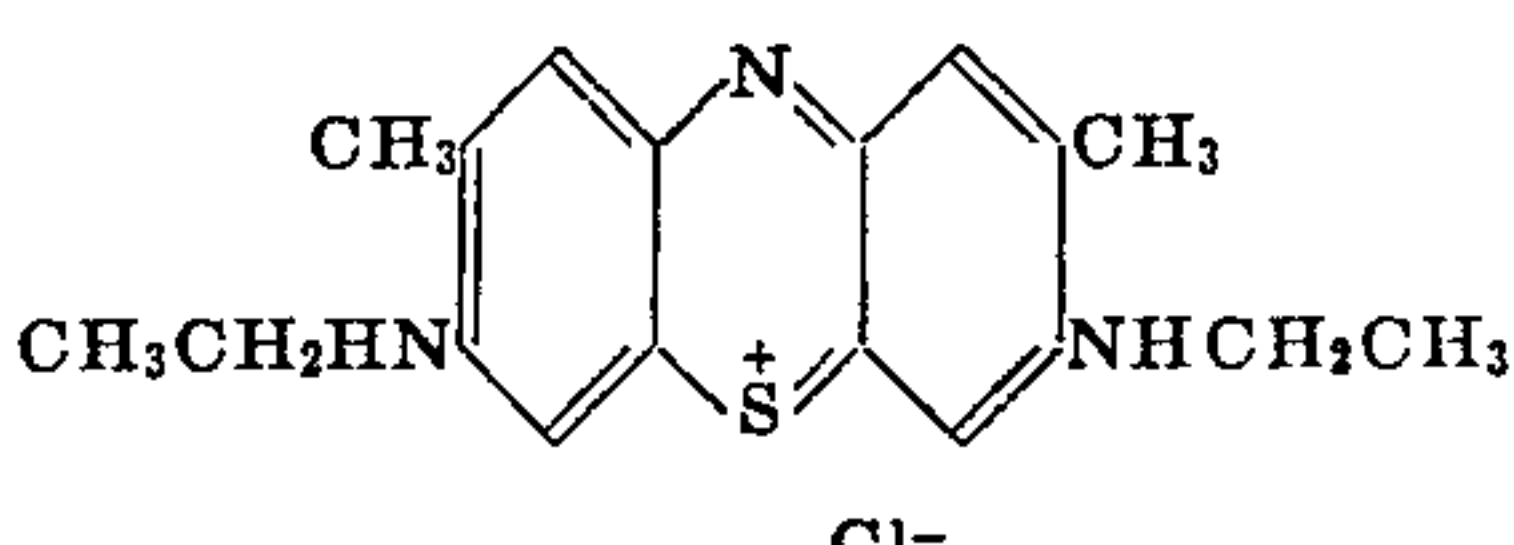
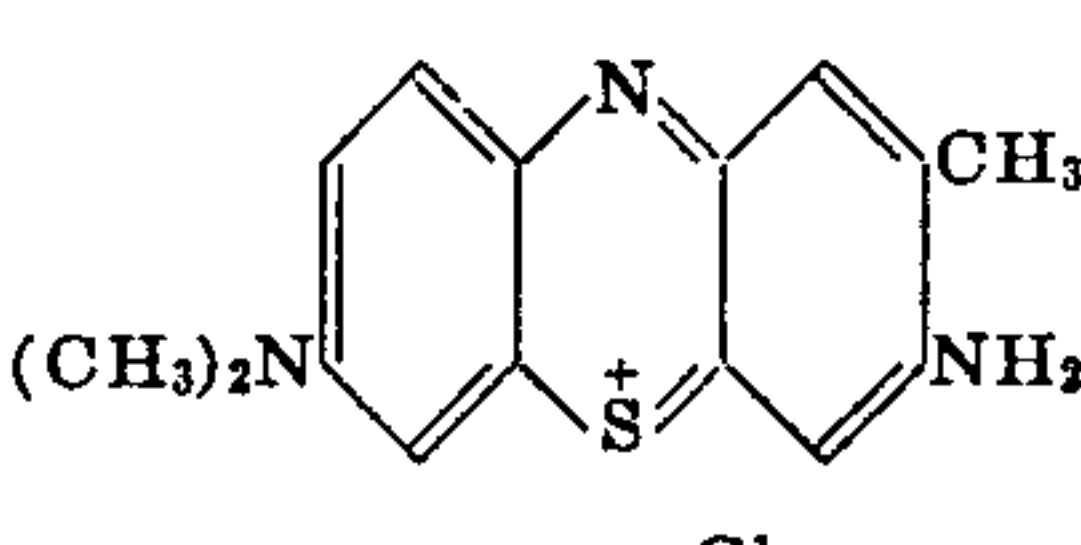
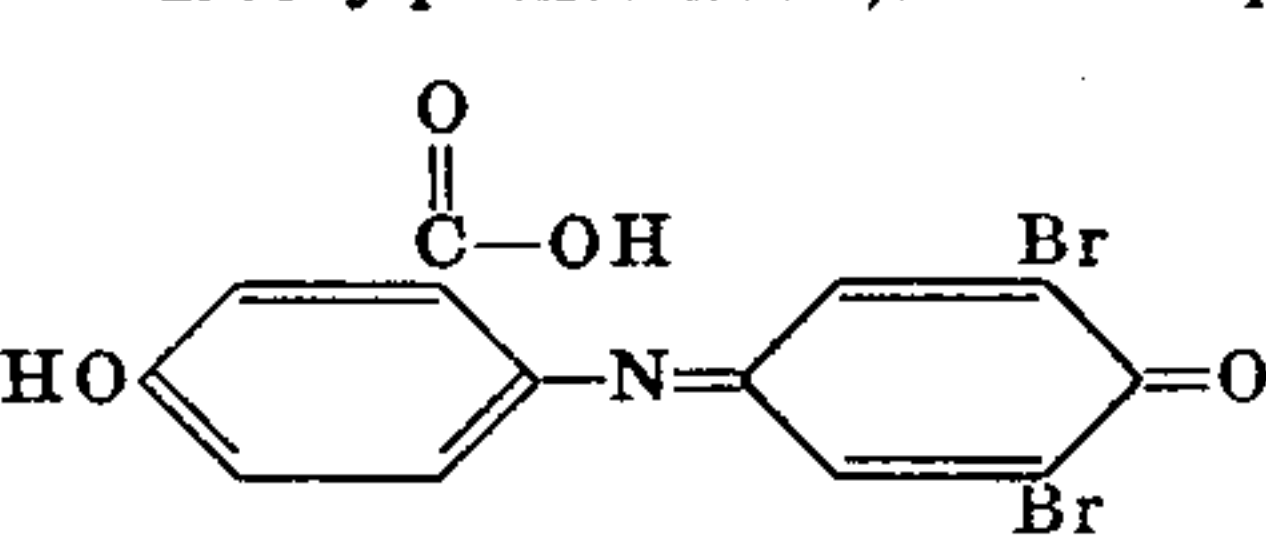
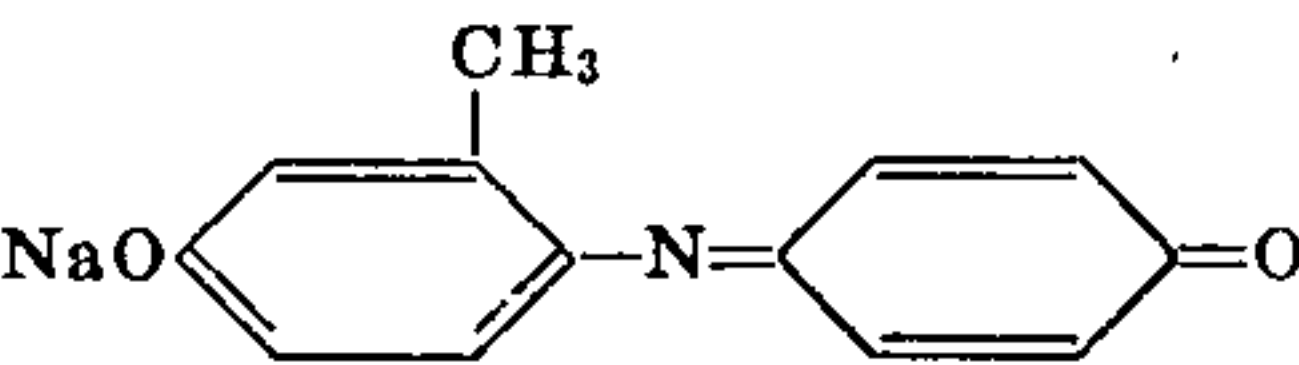
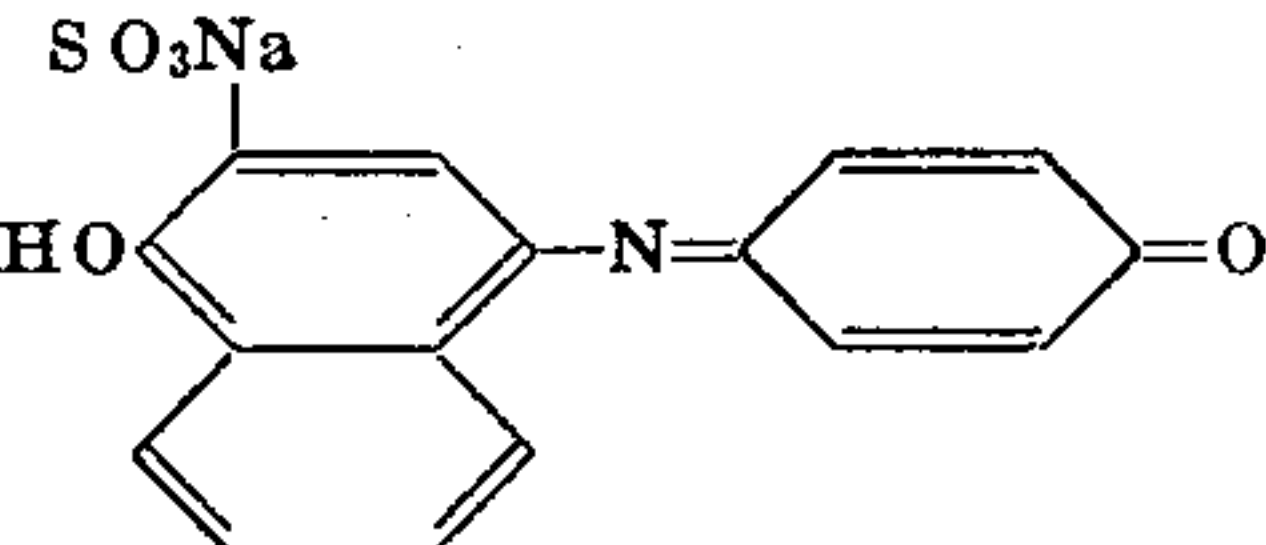
The procedure of Example 2 of this application was followed except that Quinaldine Red was substituted for Methylene Blue in one copy medium. In a second copy medium 2-(p-dimethyl-amino-styryl)-1-ethylpyridium iodide was substituted for the Methylene Blue. After 5 hours each of these two samples was processed according to the procedure of Example 1 in the application. No visible image was observed in either one of these samples.

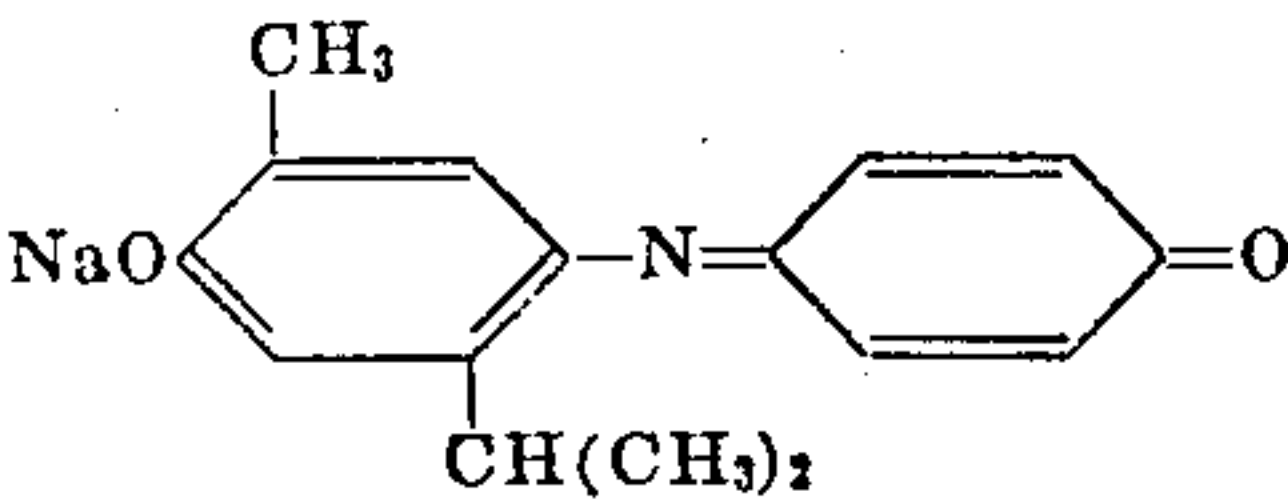
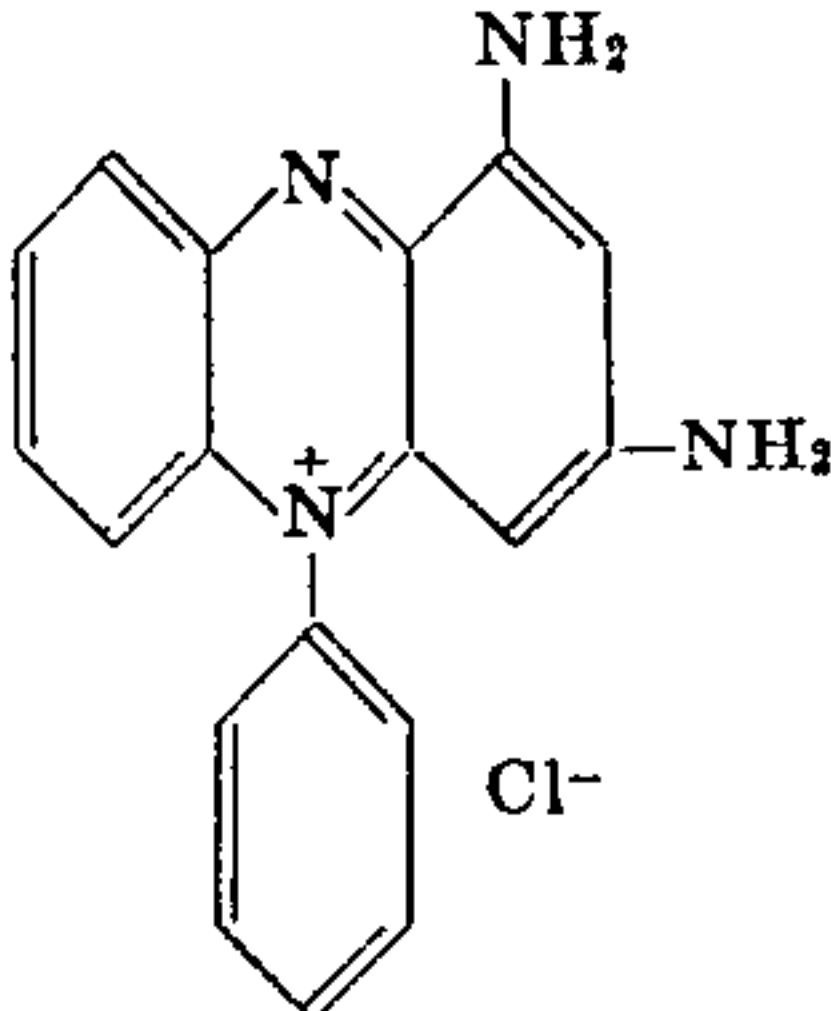
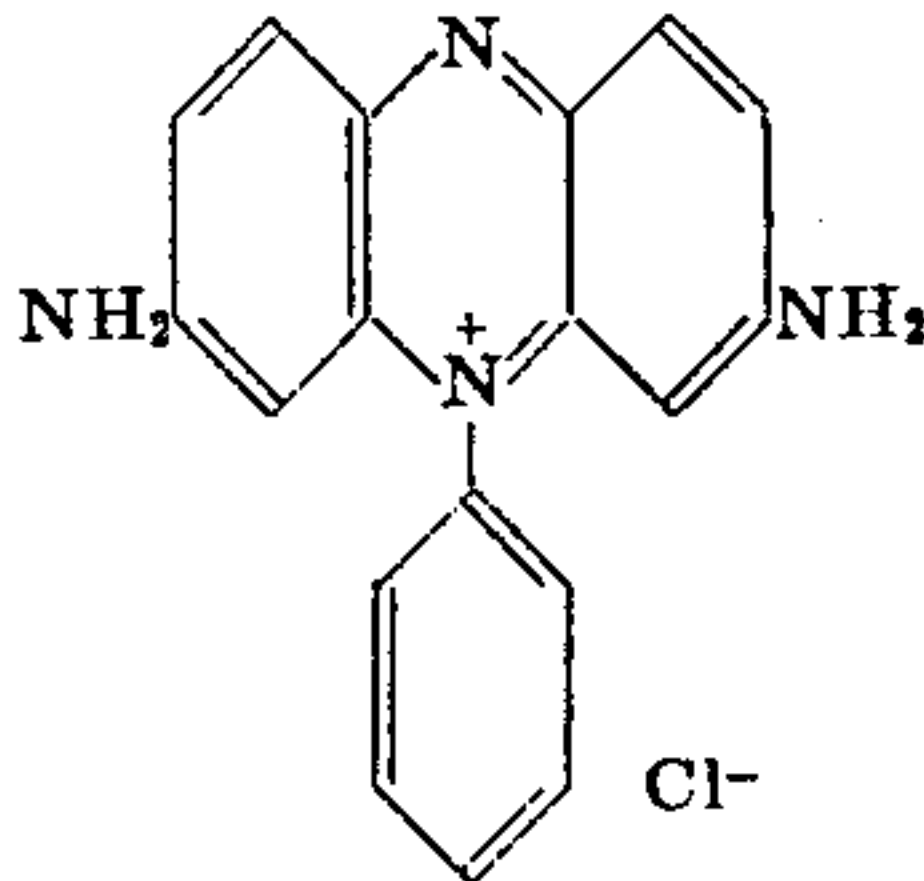
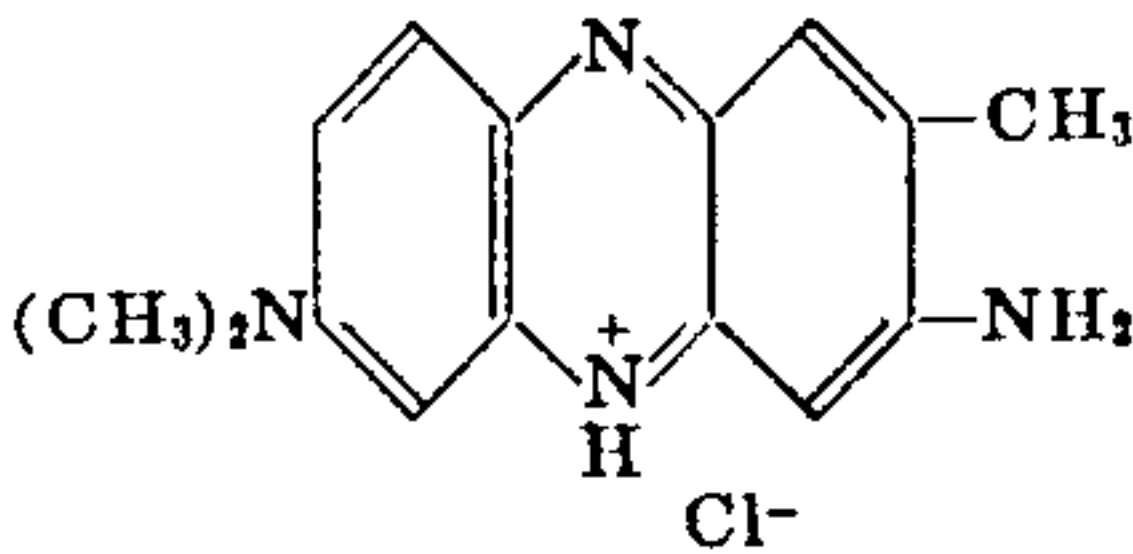
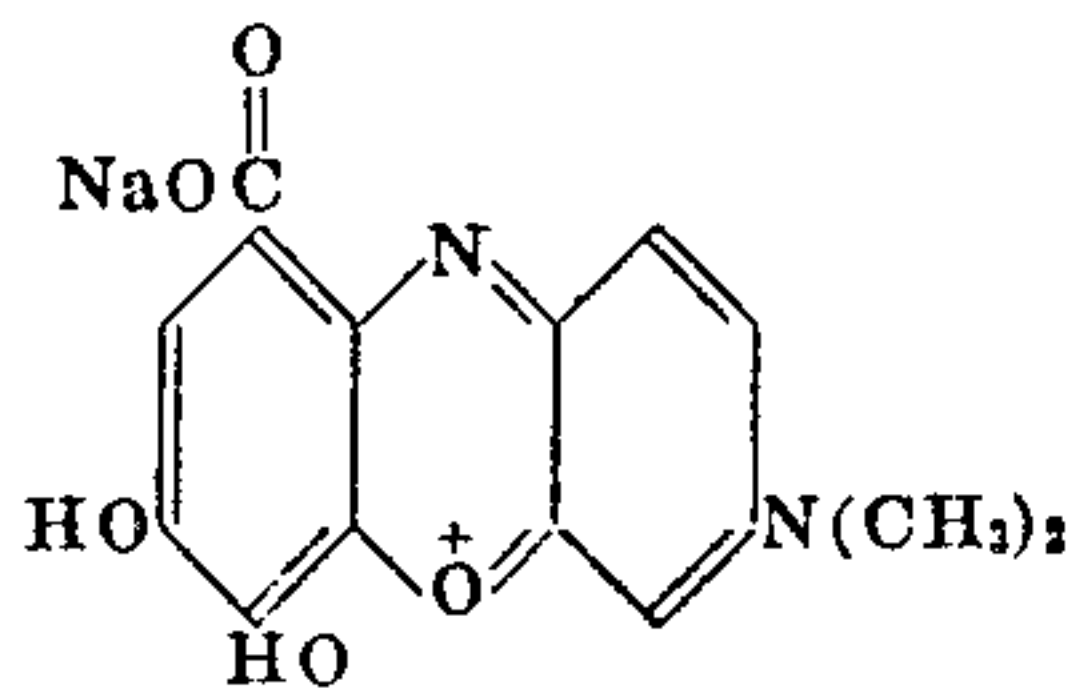
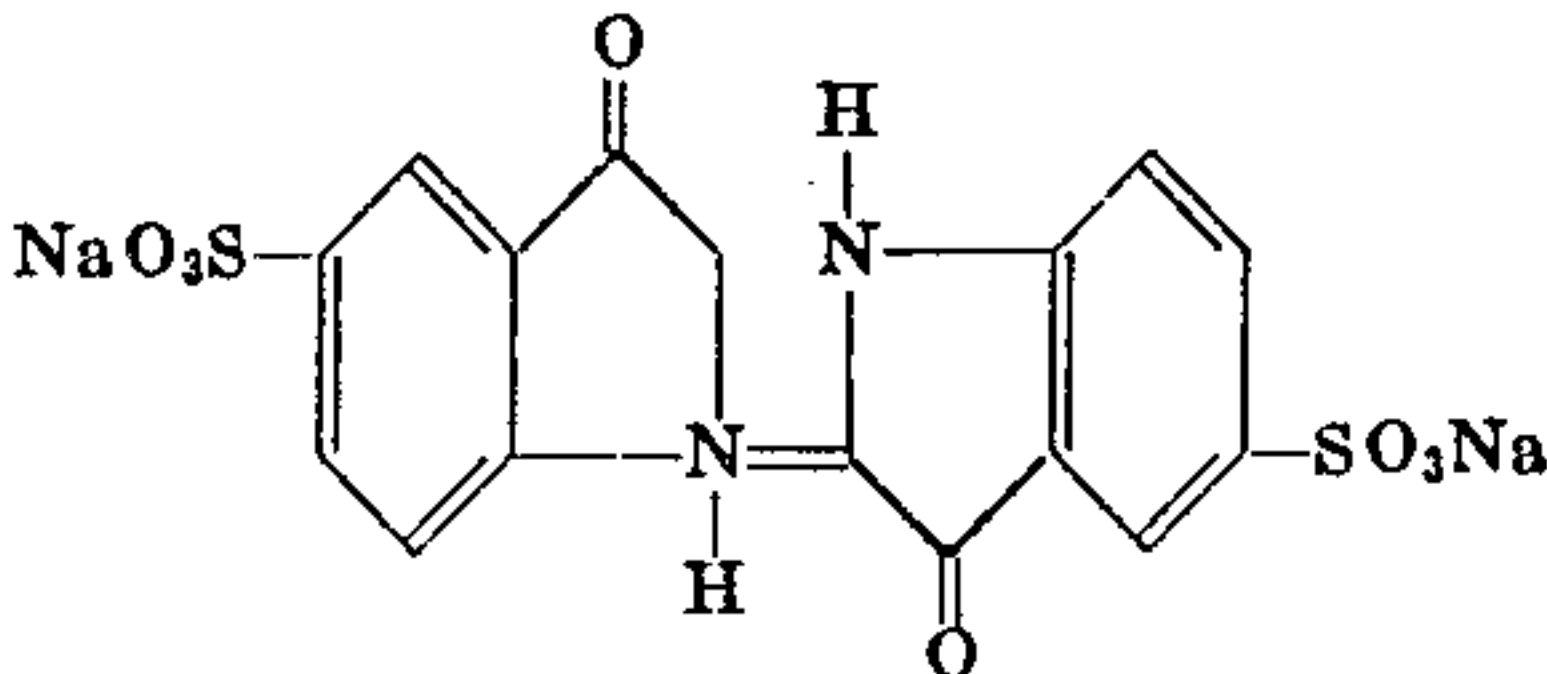
These experiments clearly indicate that these dye sensitizers fail to lengthen the life of the reversible latent image in the manner which the Methylene Blue of the application does. The redox potentials of the dyes used in this example were not of the magnitude to make them useful in this invention. However, it should be noted that the redox potential of some materials may be varied as by lowering the pH so that they may qualify as reversible oxidizing agents for this invention if the materials are otherwise acceptable.

EXAMPLES 6-19

An anodized aluminum support coated with a finely divided TiO₂ dispersed in a water permeable acrylate binder (Johnson Wax's Joncryl) is dipped in a solution of a reversible oxidizing agent. The copy medium is then allowed to dry. The thickness

of the coating is about 3×10^{-4} cm. The copy medium is then exposed to a quartz iodine lamp for 2 minutes at 30 inches to thereby produce a latent image of a reversible reducing agent. This reversible latent image is processed at different times to test the decay of the reversible latent image. The latent image life given in the following table of results is that time after exposure that a visible image can still be detected when using the following processing procedure. The processing of the reversible latent image comprises contacting the copy medium for 1.5 seconds in a silver nitrate saturated isopropyl alcohol solution followed without drying by an aqueous solution of 500 ml. of .01 N silver nitrate for 10 seconds, addition of 10 ml. of developer consisting of 9 gms. Metol, 55 gms. of nitrilotriacetic acid trisodium salt and 35 gms of citric acid per liter of water to adjust the pH to 3.5 for 30 seconds and finally contacting with 110 mls. of the developer for two minutes. The results are given in the following table:

Example Number	Reversible oxidizing agent	Latent image life
6.....	None.....	15-30 minutes.
7.....	Methylene blue zinc chloride double salt.....	Increases image decay to at least 46 hours.
		
8.....	Thionine or Lauth's violet.....	Increases decay time to at least 46 hours.
		
9.....	New Methylene Blue N.....	Increases decay time to at least 29.
		
10.....	Toluidine Blue 0.....	Increases decay time to at least 25 hours.
		
11.....	m-Carboxy-phenol-indo-2,6-dibromo-phenyl.....	Increases decay time to at least 20 hours.
		
12.....	m-Cresol indophenol sodium salt.....	Increases decay time to at least 1 hour.
		
13.....	1-naphthol-2-sodium sulphonate-indophenol sodium.....	Image decay increased to at least 46 hours.
		

Example Number	Reversible oxidizing agent	Latent image life
14.....	Carvacrol Indophenol sodium 	Increases decay time to at least 1 hour.
15.....	Pinacryptol Green 	Increases decay time to at least 47 hours.
16.....	Phenosafranine 	Increases decay time to at least 21 hours.
17.....	Neutral Red 	Increases decay time to at least 20.5 hours.
18.....	Gallocyanine 	Increases decay time to at least 25 hours.
19.....	Indigo Carmine 	Increases decay time to at least 1 hour.

EXAMPLES 20-26

An anodized brush-grained aluminum sheet is coated with a finely divided TiO_2 dispersed in a polyvinyl alcohol binder and dried. The binder has a thickness of about 3×10^{-4} cm. In all cases except the control the copy medium is then dipped in a solution of a reversible oxidizing agent and then allowed to dry. In some of the examples the reversible oxidizing agent solution is acidified by adding 1 gm. of citric acid to 200 mls. of the reversible oxidizing agent solution.

The printing plate thus produced is exposed to an image pattern from a quartz-iodide light source for two minutes at 30 inches to produce a latent image of a reversible reducing agent on the surface of the plate.

The thus exposed plate is then processed at various time intervals after exposure according to the following process: The metal plate is contacted with 10 gms. of sodium citrate to

1,000 mls. of 0.01 N AgNO_3 for 30 seconds by washing in water. The plate is then contacted for two minutes with a physical developer prepared from three stock solutions in the proportions outlined below.

65 STOCK SOLUTION NO. 1
1.0 gms. Armac 12D
1.0 gms. Synthropol
1 liter H_2O

70 STOCK SOLUTION NO. 2
Add in order given to H_2O letting each dissolve.
10.2 gms. citric acid
16.2 gms. $\text{Fe}(\text{NO}_3)_3$
39.2 gms. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$
75 250 mls. H_2O

STOCK SOLUTION NO. 3

18 gms silver nitrate
40 ml. H₂O

Solution 01	40 ml.
Solution 02	50 ml.
H ₂ O	20 ml.
Solution 03	8 ml.
TOTAL VOLUME	118 ml.

The following table of results shows the latent image stability by giving the number of steps capable of being used for printing on the developed printing plate at different time intervals after exposure:

Example number	Reversible oxidizing agent	Number of printing steps at various time intervals after exposure—									
		No delay	30 sec.	5 min.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.
20	None	5	0								
21	Thionine	2	2	2	1	0					
22	Thionine plus citric acid	8	8	8	8	8	8	7	7	6	2
23	Toluidine Blue 0	10	10	9	5	0					
24	Toluidine Blue 0 plus citric acid	8	8	8	8	8	8	8	8	7	6
25	Thionine plus toluene sulfonic acid	8	8	8	8	8	8	8	7	7	6
26	Quinone plus citric acid	9			8	7	5	3	1		

Examples 20–26 show that a reversible oxidizing agent, either alone or in combination with an acid, increases significantly the latent image stability. For example, a printing plate without a reversible oxidizing agent, as for example 20, when processed in an automatic processor wherein the end of the

PHYSICAL DEVELOPER

	Examples 27–31	Examples 32–33
5		
Solution No. 1		
Ferrous ammonium sulfate	97.3 g	78.4 g
Ferric nitrate	40.1 g	33.2 g
Citric Acid	26.0 g	80 g
Water to	1 liter	1 liter
10 Solution No. 2		
Armac 12D	1.55 g	1.0 g
Synthropol	1.55 g	1.0 g
Water to	1 liter	1 liter
15 Solution No. 3		
3 N AgNO ₃	4.17 ml.	3 N AgNO ₃
Water to	10 ml.	none
Solution No. 1	250 ml.	250 ml.
Solution No. 2	50 ml.	50 ml.
Solution No. 3	10 ml.	6 ml.
Total Volume	310 ml.	306 ml.

The film is then contacted with the standard silver halide thiosulfate solution and then fixed in water. The following table gives the latent image life by indicating the density when development occurs at different time intervals after exposure. "Good" refers to a solid, dark black image.

Example number	Reversible oxidizing agent and concentration in methanol	Density at various time intervals after exposure—					
		13 sec.	15 min.	1 hr.	2 hrs.	5 hrs.	7 hrs.
27	Control none	Good	Ghost image.				
28 ¹ (17)	Neutral Red 0.1 g./200 ml.	do	Good	Partial loss		Mostly gone	
29 ¹ (15)	Pinacryptol Green .01 g./200 ml.	do	do	Small loss		Partial loss	
30 ¹ (16)	Phenosafranine .05 g./200 ml.	do	do	Good		Ghost image	
31 ¹ (8)	Thionine or Lauth's violet 0.1 g./200 ml.	do	do	Very little loss		Partial loss	
32 ¹ (8)	Thionine or Lauth's violet .01 g./200 ml.	do	do	Good	Good	Good	Very very slight loss.
33 ¹ (10)	Toluidine Blue 0 .005 g./200 ml.	do	do	do	Partial loss.		

¹ Example number which shows corresponding structure on preceding pages.

plate is fed into the processing bath and passed gradually through the processing bath until the developing is completed may take more than 30 seconds to complete. Thus, part of the plate would have an image developed to maximum density, part of the plate would have no image at all and in between there would be varying shades of density, some which would print but most which would not. Thus, by use of the reversible oxidizing agent of this invention very large printing plates can be processed in a mechanical processor.

EXAMPLES 27–33

A polyethylene terephthalate based film is coated with a gelatin-TiO₂ emulsion wherein the TiO₂ to gelatin ratio is about 1:1 by weight. The thickness of the emulsion coating is about 3.5×10⁻⁴cm. In all cases except the control the copy medium is then dipped in a solution of a reversible oxidizing agent and then allowed to dry. In these examples the reversible oxidizing solution is acidified and the concentration of the oxidizing agent is varied to optimize the latent image stability.

The thus prepared film is exposed to an image pattern from a quartz iodide lamp 30 inches from the copy medium for 1 minute.

The thus exposed film is then processed at various time intervals after exposure according to the following process. The film is contacted with a physical developer as described below for 3 minutes.

What is claimed is:

1. In a process for recording an image pattern of radiation on a photoconductive medium containing a photoconductor which is reversibly activatable by actinic radiation, said process including at least the steps of exposing said medium to an image pattern of actinic radiation and subsequently developing said exposed medium with image-forming materials containing metal ions having at least the oxidizing power of cupric ions and a reducing agent for said metal ions, the improvement comprising:

contacting said photoconductor with a reversible oxidizing agent in an environment where the pH is lower than about 5, said reversible oxidizing agent having a redox potential (E₀) of between about 0.1 and about 0.7.

2. An improvement of claim 1 wherein said reversible oxidizing agent comprises an arylamine dye.

3. An improvement of claim 2 wherein said arylamine dye further comprises a thiazine dye.

4. An improvement of claim 2 wherein said reversibly activatable photoconductor comprises a metal oxide or a metal sulfide.

5. An improvement of claim 3 wherein said reversibly activatable photoconductor comprises titanium dioxide or zinc oxide.

6. An improvement of claim 5 wherein said reversibly activatable photoconductor comprises titanium dioxide having an average particle size of less than about 250 millimicrons.

7. An improvement of claim 6 wherein said titanium dioxide is dispersed in a solvent permeable binder.

8. An improvement of claim 7 wherein the metal ions in said image-forming materials comprise silver ions.

9. An improvement of claim 8 wherein said reversible oxidizing agent comprises Thionine or Toluidine Blue.

10. An improvement of claim 9 wherein said reversible oxidizing agent is incorporated into said photoconductive medium prior to exposure thereof.

11. An improvement of claim 10 wherein said photoconductive medium additionally has incorporated therein an acidic material which maintains the pH of said photoconductive medium at a pH below about 3.

12. A process for recording an image pattern of actinic radiation comprising:

a. contacting, in an environment having a pH below about 5, a photoconductive medium containing a photoconductor which is reversibly activatable by actinic radiation with a reversible oxidizing agent having a redox potential (E_0) of from about 0.1 to about 0.7; and,

b. exposing said photoconductive medium to an image pattern of actinic radiation to thereby reversibly activate said photoconductor.

13. A process of claim 12 including the additional step of subsequently developing a visible image in said exposed medium by contacting exposed portions with image-forming materials containing metal ions having at least the oxidizing power of cupric ions and a reducing agent for said metal ions.

14. A process of claim 13 wherein said reversible oxidizing agent comprises an arylamine dye.

15. An improvement of claim 14 wherein said arylamine dye further comprises a thiazine dye.

16. An improvement of claim 15 wherein said photoconductive medium comprises titanium dioxide or zinc oxide

dispersed in a solvent permeable binder and said medium also contains an acidic material to maintain its pH below about 3.

17. A process of claim 16 wherein the metal ions in said image-forming materials comprise silver ions.

18. A process of claim 17 wherein said reversible oxidizing agent comprises Thionine or Toluidine Blue.

19. A copy medium comprising:

a. a support; and,

b. a photosensitive photoconductive coating on said support, said photoconductive coating containing a photoconductor which is reversibly activatable by actinic radiation and a reversible oxidizing agent having a redox potential (E_0) of from about 0.1 to about 0.7, said photoconductive coating also having a pH of below about 5.

20. A copy medium of claim 19 wherein said reversible oxidizing agent comprises an arylamine dye.

21. A copy medium of claim 20 wherein said reversible oxidizing agent comprises a thiazine dye.

22. A copy medium of claim 21 wherein said photoconductive coating comprises titanium dioxide or zinc oxide dispersed in a solvent permeable binder and also contains a sufficient amount of an acidic material to maintain the pH of said photoconductive coating below about 3.

23. A copy medium of claim 22 wherein said support is conductive.

24. A copy medium of claim 23 wherein said conductive support comprises aluminum.

25. A copy medium of claim 24 wherein said photoconductive coating is less than about 0.001 cm in thickness.

26. A copy medium of claim 25 wherein said reversible oxidizing agent comprises Thionine or Toluidine Blue.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,652,276 Dated March 28, 1972

Inventor(s) Richard F. Bartlett

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

On the title page, the issue date should be changed from February 28, 1972 to March 28, 1972.

Col. 7, line 15, change "TiO" to "TiO₂".

Signed and sealed this 15th day of August 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents