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PHYSICAL DEVELOPMENT UTILIZING 1-PHENYL-3-PYRAZOLIDONE OR A BENZENE DIAMINE COMBINED WITH A POLYHYDROXYBENZENE IN ACIDIC MEDIUM

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ABSTRACT OF THE DISCLOSURE

This invention relates to physical development of a photographic reproduction system with a physical developer. The step of physical development comprises contacting an exposed photosensitive layer containing the oxidizing component of a chemical redox system, such as silver nitrate, with the reducing component of the redox system where the reducing component is a mixture of a slow-acting reducing agent and a fast-acting reducing agent. The use of a mixed reducing agent as described permits development of images of improved density and contrast because development initiates and takes place within the photosensitive layer rather than on its surface or beyond its surface as typically encountered with prior art developers. An overall process in accordance with the invention comprises selectively exposing the reproduction system to activating radiation and developing in the manner above described. A portion or all of the oxidizing component of the redox system may be contained within the photosensitive layer at the time of exposure to give a direct read-out or it is possible to apply all of the oxidizing component at a time subsequent to exposure followed by contact with the reducing portion of the redox system. A photosensitive layer comprising a photoconductor that becomes reversibly activated upon exposure to activating radiation is preferred. Titanium dioxide having a particle size less than about 250 millimicrons and which has been heated at a temperature between about 200° C. and 950° C. is the preferred photoconductor.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to the field of photographic reproduction systems and more specifically to improved development of such photographic systems.

(2) Description of the prior art

It is known in the art that photographic images can be produced by means of a "physical developer." This physical developer typically contains dissolved metal salts that may be referred to as the oxidizing component of a chemical redox system and a developing agent for the metal salts that may be referred to as the reducing component of said chemical redox system. Physical developers have several uses. For example, they may be used for increasing the density of weakly developed silver images formed from ordinary silver halide emulsion layers of the photographic reproduction systems by fixing after exposure and then developing in the physical developer. A process similar in nature is disclosed in U.S. Pat. No. 3,149,970 where an emulsion having a low concentration of silver halide is exposed and developed with a physical developer omitting the step of fixation. Another silver halide process using a physical developer is disclosed in U.S. Pat. No. 3,404,980.

An additional use of physical developers is in the development of photographic reproduction systems comprising a photoconductor that becomes reversibly activated upon exposure to activating radiation. Reproduction systems of this nature are described in detail in U.S. Pats. Nos. 3,152,903 and 3,052,541; French Pat. Nos. 345,206 and 1,245,215 and in commonly-owned co-pending U.S. application Ser. No. 199,211 filed May 14, 1962 in the name of Elliott Berman et al., now abandoned. In the aforementioned U.S. patent application, radiation-sensitive titanium dioxide functions as a photoconductive component of the media and exposure of said media to activating means such as radiant energy, electron beams or the like results in the storage of a reversible latent image pattern therein. The reversible latent image pattern exists for a limited time during which said pattern can be converted to an irreversible form and read-out visually by contacting said pattern with a suitable image forming material or physical developer such as the chemical redox system described above.

In the aforementioned U.S. and French patents, the radiation sensitive material is combined with at least one component of an image-forming material prior to exposure to activating means. For example, U.S. Pat. No. 3,152,903 discloses a system wherein the photoconductive material is used in combination with both an oxidizing agent such as silver nitrate and a reducing agent such as hydroquinone. Upon exposure to suitable activating means, a visual image is formed.

In U.S. Pat. No. 3,052,541, a similar system is disclosed wherein a photoconductor copy medium is provided comprising a photoconductive material such as titanium dioxide in combination with a reducible metal ion such as silver nitrate as an oxidizing component of a chemical redox system. The copy medium is exposed to activating radiation and then contacted with the reducing component of the redox system to produce a visible image. The visual image is formed by physical development through reduction of the silver nitrate by the reducing agent as it diffuses into the photosensitive layer. A typical reducing component of a chemical redox system is hydroquinone.

Various difficulties are encountered in attempts to develop reproduction systems of the above-described type where the oxidizing component of the chemical redox system is contained in or impregnated into the photosensitive layer. For example, hydroquinone is a relatively weak, slow-acting reducing agent. It is believed that upon immersion of the light-exposed reproduction system in a hydroquinone solution, much of the oxidizing agent diffuses out of the light-sensitive coating and into the solution before development is initiated. As a consequence, the image formed is of relatively low optical density due to a low concentration of the oxidizing agent. Alternatively, with a fast-acting reducing agent, such as Phenidone (1-phenyl-8-pyrazolidone), reduction of the oxidizing agent or development initiates immediately upon contact of the photosensitive layer with the reducing agent before the reducing agent has an opportunity to diffuse into the photosensitive coating. As a result, the developed image is not adhered to the substrate and washes off. As a consequence, the solution of the developing agent turns black and further development occurs on the surface of the photosensitive layer. Again, the result is an image of relatively low optical density.

STATEMENT OF THE INVENTION

It has now been unexpectedly found that the aforesaid difficulties can be overcome and photographic images of markedly increased optical density can be provided by contacting an exposed reproduction system of the above-described type with a reducing component of a chemical redox system that is an admixture of a fast-acting re-

ducing agent and a slow-acting reducing agent. A process in accordance with the invention would include the step of development by contacting an exposed reproduction system having a photosensitive layer containing an oxidizing component of a chemical redox system with a reducing component for said chemical redox system which reducing component is the admixture of the fast-acting reducing agent and the slow-acting reducing agent. For reasons not fully understood, the mixed reducing agent is capable of diffusing into the photosensitive layer before physical development begins and initiates development within the layer before appreciable oxidizing agent diffuses out of the photosensitive layer. Consequently, development occurs within the layer resulting in improved optical density of a developed image. Moreover, it has been unexpectedly found that the improvement in optical density is substantially greater than would be expected by arithmetically summing the results obtained using either of the reducing agents alone. The oxidizing component may be added to the photosensitive layer prior to, during or subsequent to exposure.

The preferred reproduction system comprises a substrate coated with titanium dioxide, most preferably titanium dioxide having a particle size less than about 250 millimicrons and which has been heated at a temperature between about 200° C. and 950° C. The preferred chemical redox system comprises silver nitrate as an oxidizing agent and an admixture of a dihydroxybenzene and a diaminobenzene as the reducing agent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In those reproduction systems comprising a photosensitive layer containing a photoconductor, the photoconductors or photocatalysts preferred are the metal containing photoconductors. A preferred group of such photoconductive materials are the inorganic materials such as compounds of a metal and a non-metallic element of Group VI–A of the Periodic Table* including oxides, such as zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, tin dioxide, indium trioxide; sulfides such as cadmium sulfide (CdS), zinc sulfide (ZnS) and tin disulfide (SnS_2); and selenides such as cadmium selenide (CdSe). Metal oxides are especially preferred photoconductors of this group. Titanium dioxide is a preferred metal oxide because of its unexpectedly good results. Titanium dioxide having an average particle size of less than about 250 millimicrons and which has been heated in an oxidizing atmosphere at a temperature between about 200° C. and 950° C. for from about 0.5 hour to about 30 hours is especially preferred and, more particularly, that titanium dioxide produced by high temperature pyrolysis of a titanium halide.

Also useful as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide, zinc activated zinc oxide, manganese activated zinc phosphate

$$(Zn_3(PO_4)_2)$$

a mixture of copper sulfide, antimony sulfide and magnesium oxide and cadmium borate.

While the exact mechanism by which the photoconductors work is not known, it is believed that exposure of the photoconductor or photocatalyst 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 a material has 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, the 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 in the art that it is possible to reduce the band-gap for these compounds by adding a foreign compound as an activator. This material 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 conductance band stresses the electronic configuration of the photoconductor, thereby reducing its band-gap and thus increasing its ability to release electrons in its conduction band. Phosphors almost necessarily apply the presence of such activating substances. The effect of such impurities may be such as to confer photoconductive activity upon a compound which intrinsically is non-photoconductive. The (Ca-Sr)S phosphors are believed to be an example of this group. On the other hand, excessive impurity content can interfere with a compound acting as a photoconductor as above described.

Whether a silver halide emulsion or a photoconductor as above described is used, it is preferably deposited as a photosensitive layer over an inert carrier sheet. Inert carrier sheets comprise any suitable backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier. The carrier sheet may be in any form such as, for example, sheets, ribbons, rolls and the like. This sheet may be made of any suitable material such as wood or rag content paper, pulp paper, plastics such as, for example, polyethylene terephthalate (Mylar) and cellulose acetate, cloth, metallic foil and glass. The preferred form of the carrier sheet is a thin sheet which is flexible and durable.

It is also desirable to use a binding agent to bind the photosensitive material to the carrier sheet. In general, these binders are translucent or transparent so as not to interfere with the transmission of light therethrough. Preferred binder materials are organic materials such as resins. Examples of suitable resins are butadiene-styrene copolymers, poly(alkylacrylates) such as poly-(methylmethacrylate), polyamides, polyvinyl acetate, polyvinyl alcohol, gelatin, and polyvinyl pyrrolidone.

When using a photoconductor, it should be conditioned in the dark before exposure. Such conditioning is generally conducted for a period of from 1 to 24 hours. After conditioning, the photoconductor is not exposed to light prior to its exposure to activating radiation for recording an image pattern. Radiation sources useful for recording an image pattern are generally those emitting actinic light or at least parts of the actinic light range to which the photoconductor or a dye sensitized photoconductor, if applicable, responds.

The period of exposure to the source of actinic radiation will depend upon the intensity of the light source, the particular imaging material, particular photosensitive material, the type and amount of catalyst and dye, if any, and like factors known to the art. In general, however, the exposure may vary from about 0.001 second to several minutes.

While the invention is concerned particularly with forming a negative image of a positive print, it should

*Periodic Table from Lange's Handbook of Chemistry, 9th edition, pp. 56 to 57, 1956.

be understood that the invention described herein is also applicable to such positive processes as described in U.S. Pat. No. 3,414,410 in the names of R. F. Bartlett et al. In this process, a photoconductive material is uniformly dye-sensitized and then exposed to an image pattern of activating radiation to desensitize the dye-sensitized medium to activating radiation in those portions thereof which are struck by radiation during the initial exposure, and then subsequently the thus partially-desensitized medium is exposed overall to activating radiation to activate those as-yet unexposed areas of said medium which correspond with opaque areas of the original image. By contacting with image-forming materials, a positive visual image of the original positive is produced.

Image-forming materials which are useful in this invention comprise physical developers formed within this photosensitive layer of the reproduction system from a chemical redox system comprising an oxidizing agent and a reducing agent. The oxidizing agent, for purposes of this invention, is the image-forming component of the image-forming material. Either organic or inorganic oxidizing agents may be employed as the oxidizing component of the image-forming material. Preferred oxidizing agents comprise the reducible metal ions having at least the oxidizing power of the cupric ion and include such metal ions as Ag^{+}, Hg^{+2}, Pb^{+4}, Au^{+3}, Pt^{+4}, Ni^{+2}, Sn^{+2}, Pb^{+2}, Cu^{+1}, and Cu^{+2}. Other suitable oxidizing agents useful in this invention as components on an image-forming material are permanganate (MnO_4^{-}) ion, various leuco dye materials such as disclosed in co-pending application Ser. No. 623,534 now U.S. Pat. No. 3,623,865, filed in the name of L. Case, and the like. Organic oxidizing agents include tetrazolium salts, such as tetrazolium blue and red, diphenyl carbazone and genarcyl red 6B (Methine dye).

The reducing component of the chemical redox system for purposes of this invention is a mixture of a fast-acting reducing or developing agent and a slow acting reducing or developing agent. The terms "fast-acting" and "slow-acting" are terms known in the art and relate in part to the induction period required for the developer to initiate development.

A facile method for determining whether or not a reducing or developing compound is a fast-acting or slow-acting reducing compound in accordance with the invention for any given reproduction system is to immerse the reproduction system in a 0.050 molar solution of the reducing compound in question. If the solution turns black immediately upon immersion, development is initiated too rapidly and the developer is considered a "fast-acting" developer. Alternatively, if little or no development is observed in about ten seconds, the solution is considered a "slow-acting" developer.

In a preferred embodiment of the invention, the reducing component of the image-forming material or the chemical redox system comprises a mixture of (1) a polyhydroxy benzene such as hydroquinone, catechol, pyrogallol, rescorcinol and chlorohydroquinone and (2) 1-phenyl-3-pyrazolidone(Phenidone) or an aromatic diamine such as o or p-phenylenediamine, o or p-dimethylphenylenediamine and o or p-diethylphenylenediamine. The differentiation between slow acting and fast acting developing agents as represented by polyhydroxybenzene and aromatic diamines is recognized in the art and discussed by Mees and James, The Theory of Photographic Process, New York, MacMillan, 1966, p. 283.

The ratio of the slow-acting reducing agent to the fast-acting reducing agent can vary within broad limits and is of course, dependent upon factors such as the relative reducing power of each of the components, the nature of the oxidizing component of the chemical redox system, the particular reproduction system used and the photosensitive material employed in the photosensitive layer, and the like factors known in the art. In general, the volume ratio of slow-acting reducing agent to fast-acting reducing agent may vary between 1:10 and 10:1.

As noted above, when a slow-acting reducing agent is used alone, prior to initiation of development, the oxidizing component of the chemical redox system diffuses out of the photosensitive layer. Thereafter, when development does begin, little or no oxidizing component is left in the photosensitive layer and as a result, either no image is formed or alternatively, a weak image of low optical density is formed. Alternatively, where the reducing agent is a fast-acting reducing agent, development initiates too rapidly without sufficient time for the developer to diffuse into the photosensitive layer. Consequently, development occurs on the surface of the photosensitive layer and is only weakly adhered thereto. As a result, the oxidizing component is reduced mainly in the developer solution rather than in the photosensitive layer, and again, an image of poor or low optical density is formed.

Most desirably, the developer is formulated so that the time to initiate development varies from about $\frac{1}{10}$ to 2 seconds, dependent upon the reproduction system used. This permits sufficient time for the developer to diffuse into the photosensitive layer but does not provide time for appreciable loss of the oxidizing component. In this way, physical development occurs within the photosensitive layer and the developed image is of excellent optical density.

Though pH is not critical, slightly acid solutions of the reducing component are preferred, a pH range of from 5.5 to 7.0 being most preferred.

It has been found that in accordance with this invention, the admixture of the fast-acting and slow-acting developing agents as described above, not only provide sufficient time for reducing agent to diffuse into the photosensitive coating, but in addition, it has been unexpectedly found that the improvement in optical density is substantially greater than would be expected by simply averaging the results obtained using either of the reducing agents alone.

It should be noted that developing compositions comprising hydroquinone and Phenidone mixtures are old in the art for development of silver halide emulsions. Such mixtures are disclosed in U.S. Pat. No. 3,407,043 and by Van Veelan and Willems, Photographic Science and Engineering, vol. 7, No. 2, March-April 1963, pp. 120–122. They differ from the compositions of the present invention in that they are not physical developers, they operate at a relatively high pH and require a silver solvent such as a sulfite.

The invention will be better understood by reference to the following examples.

EXAMPLE 1

A mixture of one part by weight of titanium dioxide and one part of gelatin containing about 8% solids in water is used to coat subbed cellulose triacetate film base. The so-formed photographic element is exposed for 10^{-3} seconds on an EG&G Xenon Flash Sensitometer through a Kodak No. 2 step wedge. Following exposure and a ten second pause, the exposed photographic element is immersed in a 3 N solution of silver nitrate and then a 0.050 molar solution of hydroquinone for 30 seconds, thereafter, fixed in a thiosulfate solution for three minutes, washed in water for twenty minutes and dried. No visual image is apparent on the surface of the developed photographic element.

EXAMPLES 2 TO 7

The procedure of Example 1 is repeated using various combinations of hydroquinone and N,N'dimethyl-p-phenyleneamine sulfate in place of hydroquinone. D Log E curves were prepared for each of the developed samples and both gamma and speed (measured at a net density of 1.0) are measured from each of the D Log E curves. The

results and developer formulations are set forth in the following table:

Ex. No.	Mole percent Hydroquinone [1]	Mole percent Diamine [1]	Gamma Expected [2]	Gamma Found	Speed [2] Expected	Speed [2] Found
2	0	100	1.51	1.51	3.6	3.6
3	25	75	1.13	1.43	2.6	3.2
4	50	50	0.76	1.62	1.7	2.8
5	75	25	0.38	2.08	0.8	4.5
6	99	1	0.02	0.03	0	0
7	100	0	0	0	0	0

[1] The total concentration of the reducing agent in the developer is maintained at 0.050 mole per liter.
[2] Arithmetic sum of each of the developers used alone.

From the above table, it can be seen that the optimum molar ratio of hydroquinone to the diamine is 3 to 1 when the total developing agent concentration is 0.050 molar. Obviously, different optimum ratios would be expected for different total developing agent concentrations, or changes in the viscosity of the developer.

EXAMPLES 8 TO 12

The procedure of the preceding examples is repeated using a Phenidone-hydroquinone developer mixture having a total developer concentration of 0.0247 mole per liter. The composition of the developer and the results obtained are set forth in the following table:

Example number	Mole percent Hydroquinone	Mole percent Phenidone	Speed (relative) [1] Expected [2]	Speed (relative) [1] Found
8	0	100	8.3	8.3
9	25	75	5.5	9.3
10	50	50	2.8	6.2
11	75	25	0	0
12	100	0	0	0

[1] Measured at a net density of 0.03.
[2] Arithmetic sum based on performance of each developer separately.

Gamma was not measured for the preceding examples inasmuch as the D Log E curves are not linear. From the above, it can be sen that the optimum molar ratio of hydroquinone to Phenidone under the specific developing conditions used is 1 to 3. The addition of hydroquinone, which develops no image when used alone to Phenidone increased the photographic speed obtained.

EXAMPLES 13 TO 15

The procedure of the preceding examples was repeated substituting a 1.5 N silver nitrate solution for the 3 N silver nitrate solution previously used. Developer formulations and results obtained are set forth in the following table:

Example number	Mole percent Hydroquinone	Mole percent Phenidone	Speed (relative) [1] Expected [2]	Speed (relative) [1] Found
13	0	100	13.0	13.0
14	75	25	3.3	9.1
15	100	0	0	0

[1] Measured at net density 0.30.
[2] Arithmetic sum of each developer separately.

From the above, it can be seen that the optimum ratio of fast-acting developer to slow-acting developer is dependent upon the reproduction system used and that by variation in the strength of the oxidizing agent, the ratio can be materially altered.

I claim:

1. In a method for the physical development of a photographic image reproduction medium comprising a photoconductor, said method comprising imagewise exposing said medium, contacting said medium with an oxidizing component of an image-forming chemical redox system comprising a solution of silver ions, and then contacting said medium with the reducing component for said redox system, the improvement wherein the reducing component comprises a mixture of a fast-acting reducing agent comprising 1-phenyl-3-pyrazolidone or a benzene diamine and a slow-acting reducing agent comprising a polyhydroxybenzene in amounts whereby the reducing component is capable of initiating development of the exposed image reproduction medium and said reducing agent component being at a pH from about 5.5 to about 7.0.

2. The method of claim 1 where the photographic image reproduction medium comprises a substrate and a photosensitive layer comprising a photoconductor that becomes reversibly activated upon exposure to a source of activating radiation.

3. The method of claim 1 wherein the photographic image reproduction medium comprises a substrate and a photosensitive layer thereon.

4. The method of claim 1 where the volume ratio of fast-acting reducing agent to slow-acting reducing agent in said reducing component varies between about 1:10 and 10:1.

5. The method of claim 1 where the polyhydroxybenzene is selected from the group consisting of hydroquinone, catechol, pyrogallol, rescorcinol and chlorohydroquinone.

6. The method of claim 1 where the total reducing agent concentration varies between 0.01 to 1 molar in aqueous solution.

7. The method of claim 1 where the reducing component of the redox system is a mixture of hydroquinone and N,N'-dimethyl-p-phenylenediamine.

8. The method of claim 1 where the reducing component of the redox system is a mixture of hydroquinone and 1-phenyl-3-pyrazolidone.

9. The method of claim 2 where the radiation-activatable photoconductor is a metal oxide.

10. The method of claim 9 where the radiation-activatable photoconductor is titanium dioxide.

11. The method of claim 1 where the silver ion is derived from a silver nitrate solution.

12. In a method for the physical development of an imagewise exposed reproduction medium comprising a layer of radiation-activatable metal oxide photoconductor impregnated with a solution of a reducible silver ion which comprises the oxidizing component of an image-forming chemical redox system, said method comprising the step of contacting said reproduction medium prior to, during or subsequent to exposure with the reducing component of said redox system, the improvement wherein the reducing component comprises a mixture of a fast-acting reducing agent comprising 1-phenyl-3-pyrazolidone or a benzene diamine and a slow-acting reducing agent comprising a polyhydroxybenzene, said fast-acting reducing agent and said slow-acting reducing agent being present in amounts whereby the reducing component of the redox system is capable of initiating development within the layer of metal oxide radiation-activatable photoconductor and said reducing agent component being at a slightly acid pH.

13. The method of claim 12 where the volume ratio of fast-acting reducing agent to slow-acting reducing agent in said reducing component varies between about 1:10 and 10:1.

14. The method of claim 12 where the fast-acting reducing agent and the slow-acting reducing agent are present in the reducing component of the redox system in amounts whereby development is initiated within from about 1/10 to 2 seconds after contact of the exposed image reproduction system with the reducing component and the pH of the solution of reducing component varies between 5.5 and 7.0.

15. The method of claim 12 where the metal oxide photoconductor is titanium dioxide.

16. The process of claim 12 where the polyhydroxybenzene is selected from the group consisting of hydroquinone, catechol, pyrogallol, resorcinol and chlorohydroquinone.

17. The process of claim 15 where the total reducing agent concentration in the reducing component varies between 0.01 and 1 mole per liter in aqueous solution.

18. The process of claim 15 where the reducing component comprises a mixture of hydroquinone and N,N'-dimethyl-p-phenylene diamine.

19. The method of claim 15 where the reducing component comprises a mixture of hydroquinone and 1-phenyl-3-pyrazolidone.

20. In a method for the physical development of an imagewise exposed reproduction medium comprising a layer of radiation activatable titanium dioxide photoconductor containing a solution of silver ions which comprises the oxidizing component of an image forming chemical redox system, said method comprising the step of contacting the reproduction medium prior to, during or subsequent to exposure with the reducing component of said redox system, the improvement wherein the reducing component comprises a mixture of a fast-acting reducing agent comprising 1-phenyl-3-pyrazolidone or a benzene diamine and a slow-acting reducing agent comprising a polyhydroxybenzene, said fast-acting reducing agent and said slow-acting reducing agent being present in a volume ratio of between about 1:10 and 10:1 and being present in aqueous solution in an amount varying between 0.1 and 1.0 molar.

21. The method of claim 20 where the reducing component of the redox system comprises a mixture of hydroquinone and 1-phenyl-3-pyrazolidone.

22. The method of claim 20 where the reducing component of the redox system comprises a mixture of hydroquinone and N,N'-dimethyl-p-phenylene diamine.

23. The method of claim 20 where the titanium dioxide has a particle size less than about 250 millimicrons and has been heated at a temperature between about 200° C. and 950° C. and the silver ion is impregnated in the titanium dioxide in the form of a silver nitrate solution.

24. In a photographic reproduction medium comprising a substrate and a photosensitive layer containing a photoconductor, said photosensitive layer containing a physical developer comprising a solution of reducible silver ions and a reducing agent composition for said metal ions, the improvement wherein the reducing agent composition comprises a mixture of a fast-acting reducing agent comprising 1-phenyl-3-pyrazolidone or a benzene diamine and a slow-acting reducing agent comprising a polyhydroxybenzene, the volume ratio of said fast-acting reducing agent and a slow-acting reducing agent varying between 1:10 to 10:1.

25. The reproduction system of claim 24 where the photosensitive layer comprises a photoconductor that becomes reversibly activated upon exposure to a source of activating radiation.

26. The reproduction system of claim 24 where the photoconductor is titanium dioxide.

27. The reproduction system of claim 25 where the solution of the reducible metal ions is a silver nitrate solution.

28. The reproduction system of claim 25 where the total reducing agent concentration varies between 0.01 to 1 molar in aqueous solution and the pH of the reducing solution varies between 5.5 and 7.0.

29. The reproduction system of claim 25 where the reducing agent is a mixture of hydroquinone and N,N'-dimethyl-p-phenylene diamine.

30. The reproduction system of claim 25 where the reducing agent is a mixture of hydroquinone and 1-phenyl-3-pyrazolidone.

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