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PHOTOGRAPHIC PRODUCTS AND PROCESSES

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No Drawing. Continuation of application Serial No. 478,193, December 28, 1954. This application July 10, 1957, Serial No. 670,859

24 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to products and processes for the development of photosensitive silver halide elements.

It is one object of the present invention to provide novel processes for the development of silver halide emulsions, in which the developing agent is capable of developing a photographic latent image and imparting a reversed or positive colored image of said latent image to a superposed image-receiving element.

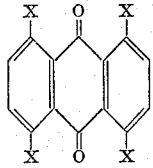
Another object is to provide novel processes for the development of silver halide emulsions, wherein the unoxidized developing agent is utilized to provide a colored image.

A further object is to provide novel products and compositions suitable for use in preparing monochromatic and multichromatic photographic images.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

The objects of this invention may be accomplished by the use of a compound which, in its unoxidized form, is a silver halide developer, and in its oxidized form is colored, and in particular by the use of the leuco form of an anthraquinone compound substituted in at least two of the alpha positions by amino or hydroxyl groups. Such compounds may be represented as compounds of the formula:



to which one mole of hydrogen has been added, wherein at least two X's are hydroxyl or amino groups, and the remaining X's are hydrogen, hydroxyl or amino groups.

Suitable leuco compounds within the scope of this invention include leucoquinizarin (i.e., leuco 1,4-dihydroxy-anthraquinone), leuco 1,4 - dihydroxy - 5,8-diamino-anthraquinone, and leuco 1,4,5,8 - tetrahydroxy-anthraquinone.

The photographic processes and compositions disclosed herein are particularly useful in the treatment of a latent image present in a photosensitive element, such as an exposed silver halide emulsion, whereby a positive dye image thereof may be imparted to another element, herein referred to as an image-carrying or image-receiving element.

U.S. Letters Patent Nos. 2,559,643 and 2,647,049 to Edwin H. Land disclose examples of diffusion transfer reversal processes wherein a photographic material, such as a photosensitive element comprising an exposed-silver halide emulsion layer containing a latent image, is processed to impart to an image-carrying or image-receiving element a reversed or positive dye image of said latent image by permeating into said emulsion layer a suitable liquid processing composition and bringing said photosensitive element into superposed relationship with an appropriate image-receiving element.

In carrying out the process of this invention, a photosensitive element comprising a silver halide emulsion is exposed and a liquid processing composition applied thereto, as by immersing, coating, spraying, flowing, etc., in the dark. In a preferred embodiment, the photosensitive element contains a layer of the leuco compound and the liquid processing composition is applied to the exposed photosensitive element in a uniform layer as this element is brought into superposed relationship with the image-receiving element. Assuming for purposes of illustration, that the leuco compound is leucoquinizarin, the liquid processing composition permeates the emulsion and provides a solution of leucoquinizarin substantially uniformly distributed therein. As the leucoquinizarin develops the latent image to silver, its oxidation product is immobilized or precipitated in situ with said silver. This immobilization is apparently primarily due to a change in the solubility characteristics of leucoquinizarin upon oxidation, and especially as regards its solubility in alkaline solution. It may also be due, in part, to a tanning effect on the emulsion by the oxidized developing agent. The unoxidized leucoquinizarin retains its solubility in the liquid processing composition, thereby providing an imagewise distribution of unoxidized leucoquinizarin, at least part of which is transferred, by imbibition, to a superposed image-receiving element, said transfer substantially excluding silver or oxidized leucoquinizarin. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized leucoquinizarin without appreciably disturbing its image-wise distribution. The transferred, unoxidized leucoquinizarin is oxidized to give a reversed or positive, colored image of the developed negative image. The image-receiving element may contain agents adapted to oxidize the diffused, unoxidized leucoquinizarin, and also may contain agents, e.g., mordants, to fix the oxidized or unoxidized leucoquinizarin. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of the imbibition period.

The leuco compound may be disposed in the liquid processing composition, in the image-receiving element, or in the photosensitive element; for example, in, on, or behind the silver halide emulsion layer. When employed in either element, the leuco compound becomes solubilized by the liquid processing composition as it permeates the element. In a preferred embodiment, the coating or layer of leuco compound is incorporated in the photosensitive element, preferably behind the silver halide emulsion layer, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the photosensitive element is exposed. Placing the leuco compound behind the emulsion layer has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the leuco compound. Where the leuco compound is employed as a layer within the

photosensitive element, it may be applied by using a coating solution containing about 0.5 to 8%, by weight, of leucoquinizarin. Similar concentrations may be used if leucoquinizarin is utilized as a component of the liquid processing composition.

The liquid processing composition referred to above comprises at least an aqueous solution of an alkaline material, such as diethylamine, sodium hydroxide or sodium carbonate. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it may also include a viscosity-increasing compound constituting film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric water-soluble ether which is inert to an alkaline solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents may be employed whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time. The liquid processing composition may also be applied prior to exposure, in accordance with the disclosure in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955.

The unoxidized leuco compound which diffuses to the image-receiving element is oxidized to provide the desired positive dye image. This oxidation may be effected by merely exposing the stripped image-receiving element to the air. In a preferred embodiment, the image-receiving element has incorporated therein an oxidizing agent for the purpose of speeding up dye image formation, and providing full image density immediately upon stripping. The incorporation of an oxidizing agent in the image-receiving element for the purpose of oxidizing unreacted developing agent permeated therein is described in the previously mentioned U.S. Patent No. 2,559,643. As examples of suitable oxidizing agents, mention may be made of peroxy compounds such as sodium or potassium perborate, and compounds having polyvalent metallic elements in higher valent form, such as copper, iron or cerium, wherein the metallic element is in higher valent form. Examples of these latter mentioned agents are cupric salts such as cupric sulfate. Other suitable oxidizing agents include benzoyl peroxide and dicyanobenzoquinone.

The following examples are intended to illustrate the use of leuco compounds in accordance with this invention, and are given as illustrations only:

Example 1

A baryta base is coated with a solution comprising 1.9 g. of leucoquinizarin dissolved in 100 cc. of a 4% aqueous cellulose acetate hydrogen phthalate solution. After this coating has dried, a silver iodobromide emulsion is then applied. The thus coated baryta base is exposed and wetted with a liquid processing composition comprising:

Water	cc.	100
Sodium carboxymethyl cellulose	g.	4.5
Sodium hydroxide	g.	2.0
Phenylethyl alcohol	cc.	1.5
Metol (p-methylaminophenol)	g.	0.05

as the exposed baryta base is brought into superposed relationship with an image-receiving element. The image-receiving element is a polyvinyl butyral coated baryta paper coated with a solution comprising .6% benzoyl peroxide in a solution comprising 1 part by weight of "Vinylite 28–18" (trade name of Bakelite Division, Carbide and Carbon Chemicals Corporation for partially hydrolyzed polyvinyl acetate, 28% solid content) and 4 parts of acetone . After an imbibition period of approximately one minute, the image-receiving element is separated and is found to contain a yellow, positive dye image of the photographed subject.

Example 2

The procedure described in Example 1 is repeated using 3% of leuco 1,4-dihydroxy-5,8-diamino-anthraquinone in place of the leucoquinizarin. After exposure, the photosensitive element is processed with an aqueous solution comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	0.85
1-phenyl-3-pyrazolidone	0.2

and an image-receiving element prepared by coating a cellulose acetate-coated baryta paper with a solution comprising 4% Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware for N-methoxymethyl polyhexamethylene adipamide). A cyan positive image is obtained by stripping the image-receiving element, after an imbibition period of approximately one minute, and oxidizing the transferred leuco 1,4-dihydroxy-5,8-diamino-anthraquinone.

Example 3

A blue-purple positive image is obtained by repeating the procedure of Example 2 using 3% of leuco 1,4,5,8-tetrahydroxy-anthraquinone and a processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	1.5
1-phenyl-3-pyrazolidone	0.2

It will be noted that a small amount of an auxiliary or accelerating developing agent, such as metol or a 3-pyrazolidone, preferably 1-phenyl-3-pyrazolidone, may be, and in the above examples is, included in the liquid processing composition. This auxiliary developing agent serves to accelerate and possibly initiate development. It may also be included, at least in part, in the photosensitive element. Some of the leuco compound may be oxidized as a result of an energy transfer reaction with oxidized auxiliary developer.

It has been found that the color of the oxidized leuco compound which forms the positive colored image may be affected by changes in the pH of that portion of the image-receiving element. For example, the positive image obtained using leucoquinizarin is yellow when this pH is acid or substantially neutral, whereas it is light purple when a 1% sodium hydroxide solution is applied to the positive image. It is therefore necessary to assure that the environment in which the transferred and unoxidized leuco compound is deposited has, or is capable of attaining the requisite pH value affording the desired color to the oxidized leuco compound. This may be accomplished by use of a volatile basic compound, such as diethylamine, in the liquid processing composition. If sodium hydroxide is utilized in the processing liquid, it becomes carbonated after processing and by contact with the air, and this is effective to provide the desired pH change. Further control of the pH of the positive dye image may be had by utilizing an image-receiving element which is difficultly penetrable by alkali, for example an appropriate nylon such as N-methoxymethyl polyhexamethylene adipamide, or by the use of an image-receiving element in which an acid or an acid-forming compound, for example oleic acid, has been incorporated.

It will be apparent that by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain a colored reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special

photographic materials, for example film material of the type containing two or more photosensitized elements associated with a suitable number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate developing agents suitable to impart the desired subtractive colors being incorporated in the photosensitized element or in the liquid processing composition. Examples of such photographic materials are disclosed in the previously mentioned U.S. Patent No. 2,647,049 to Edwin H. Land.

The inventive concepts herein set forth are also adaptable to the formation of color images in accordance with the photographic products and processes disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, now abandoned in favor of a continuation-in-part thereof, Serial No. 748,421, filed July 14, 1958, and also those set forth in the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954.

In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

This application is in part a continuation of our copending application, Serial No. 478,193, filed December 28, 1954, now abandoned.

Since certain changes may be made in the above processes and products without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

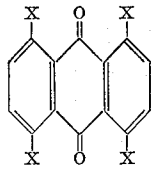
What is claimed is:

1. The process of developing a latent image contained in an exposed silver halide emulsion which comprises developing said exposed silver halide emulsion with a developer composition comprising an aqueous alkaline solution of leucoquinizarin.

2. The process of developing a latent image contained in an exposed silver halide emulsion which comprises developing said exposed silver halide emulsion with a developer composition comprising leuco 1,4-dihydroxy-5,8-diamino-anthraquinone.

3. The process of developing a latent image contained in an exposed silver halide emulsion which comprises developing said exposed silver halide emulsion with a developer composition comprising leuco 1,4,5,8-tetrahydroxy-anthraquinone.

4. In a process of forming a photographic image in color, the steps which comprise developing a latent image contained in an exposed silver halide emulsion with an aqueous alkaline solution of a leuco compound selected from the class consisting of compounds of the formula:



to which a mole of hydrogen has been added, and wherein at least two of said X's are selected from the group consisting of hydroxyl and amino groups and the remaining X's are hydrogen to provide, in said emulsion, a predetermined distribution of unoxidized leuco compound, transferring at least part of said distribution of unoxidized leuco compound by inhibition from said emulsion to an image-receiving element in superposed relationship with said emulsion and oxidizing the diffused, transferred, unoxidized leuco compound to impart to said image-receiving element a reversed positive dye image of the developed image.

5. The process as defined in claim 4 wherein said leuco compound is leucoquinizarin.

6. The process as defined in claim 4 wherein said leuco compound is leuco 1,4-dihydroxy-5,8-diamino-anthraquinone.

7. The process as defined in claim 4 wherein said leuco compound is 1,4,5,8-tetrahydroxy-anthraquinone.

8. The process as defined in claim 4 wherein said leuco compound is disposed, prior to exposure, in a photosensitive element containing said emulsion, and the solution containing said leuco compound is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said leuco compound.

9. The process as defined in claim 8 wherein said liquid is introduced by being spread in a substantially uniform layer between said photosensitive element and said image-receiving element as said elements are brought into superposed relationship.

10. The process as defined in claim 9 wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving element.

11. The process as defined in claim 4 wherein said leuco compound is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

12. The process as defined in claim 4 wherein said diffused, transferred, unoxidized leuco compound is oxidized by exposure to air.

13. The process as defined in claim 4 wherein said diffused, transferred, unoxidized leuco compound is oxidized by an oxidizing agent incorporated in said image-receiving element.

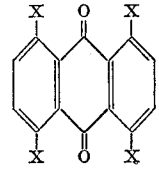
14. A process as defined in claim 13 wherein said oxidizing agent is benzoyl peroxide.

15. The process as defined in claim 4 wherein said development is effected in the presence of a small amount of an auxiliary developing agent.

16. The process as defined in claim 15 wherein said auxiliary developing agent is 1-phenyl-3-pyrazolidone.

17. The process as defined in claim 15 wherein said auxiliary developing agent is para-methyl-aminophenol.

18. The process of developing a latent image contained in an exposed silver halide emulsion which comprises developing said exposed silver halide emulsion with a developer composition comprising an aqueous alkaline solution of a leuco compound selected from the class consisting of compounds of the formula:



to which a mole of hydrogen has been added, and wherein at least two of said X's are selected from the group consisting of hydroxyl and amino groups and the remaining X's are hydrogen.

19. A photographic product as defined in claim 18 including an image-receiving layer adapted to be superposed with said silver halide emulsion.

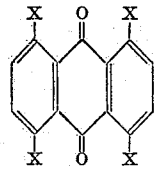
20. A photographic product comprising a plurality of layers including a layer containing a silver halide emulsion, at least one of said layers containing leucoquinizarin.

21. A photographic product comprising a plurality of layers including a layer containing a silver halide emulsion, at least one of said layers containing leuco 1,4-dihydroxy-5,8-diamino-anthraquinone.

22. A photographic product comprising a plurality of layers including a layer containing a silver halide emulsion, at least one of said layers containing leuco 1,4,5,8-tetrahydroxy-anthraquinone.

23. A photographic product comprising a plurality of layers including a layer containing a silver halide emulsion, at least one of said layers containing a leuco com-

pound selected from the class consisting of compounds of the formula:



to which a mole of hydrogen has been added, and wherein at least two of said X's are selected from the group

consisting of hydroxyl and amino groups and the remaining X's are hydrogen.

24. A photographic product as defined in claim 23 wherein said leuco compound is contained in said silver halide emulsion layer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,206,126	Schinzel	July 2, 1940
2,449,388	Kendall et al.	Sept. 14, 1948

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,892,710 June 30, 1959

Marilyn R. Cohler et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 4, after "exposed" strike out the hyphen; column 6, line 59, for the claim reference numeral "18" read -- 23 --.

Signed and sealed this 8th day of December 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

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