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2,992,105

# PHOTOGRAPHIC DIFFUSION TRANSFER REVERSAL PROCESSES

Richard S. Corley, Wellesley Hills, and Milton Green, Newton Highlands, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

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12 Claims. (Cl. 96—29)

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

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

Another object is to provide novel processes and compositions 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, processes 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 and compositions 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 certain compounds hereinafter described, which possess the ability to function as photographic developing agents, and whose oxidation products are dyes. These compounds will be referred to hereinafter as leuco developing agents.

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 a leuco developing agent, 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. The liquid processing composition



permeates the emulsion and provides a solution of leuco developing agent substantially uniformly distributed therein. As the leuco developing agent develops the latent image to silver, its oxidation product is immobilized or precipitated in situ with said silver. This immobilization is apparently due, at least in part, to a change in the solubility characteristics of the leuco developing agent 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 leuco developing agent. The unoxidized leuco developing agent retains its solubility in the liquid processing composition, thereby providing an imagewise distribution of unoxidized leuco developing agent, at least part of which is transferred, by imbibition, to a superposed image-receiving element containing a layer of a dyeable material, said transfer substantially excluding silver or oxidized leuco developing agent. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized leuco developing agent without appreciably disturbing its imagewise distribution. The unoxidized leuco developing agent which diffuses to the image-receiving element 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, mordant or otherwise fix the diffused, unoxidized leuco developing agent. 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 image-receiving layer is stripped from the photosensitive layer at the end of the imbibition period.

The leuco developing agents disclosed herein may be disposed in the liquid processing composition, 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 developing agent becomes solubilized by the liquid processing composition as it permeates the element. In a preferred embodiment, the coating or layer of the leuco developing agent 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 developing agent behind the emulsion layer has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action if the leuco developing agent is colored. If the leuco developing agent is colorless, it may be incorporated in the silver halide emulsion without adverse light-filtering effect. Where the leuco developing agent 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 the leuco developing agent. Similar concentrations may be used if the leuco developing agent is utilized as a component of the liquid processing composition.

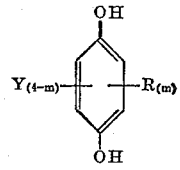
The liquid processing composition referred to above comprises at least an aqueous solution of an alkaline material, such as diethylamine, sodium hydroxide or sodium carbonate. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin 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 unoxidized leuco developing agent which diffuses to the image-receiving element is oxidized to provide the desired positive dye image. When the leuco developing agent is readily oxidizable, this oxidation may be effected by merely exposing the stripped image-receiving element to the air. In one embodiment, the image-receiving element may have 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 an 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. Another suitable oxidizing agent is benzoyl peroxide.

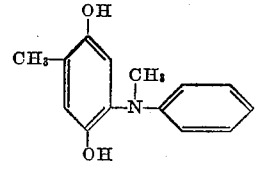
The compounds which may be used to accomplish the objects of this invention may be referred to as arylamino- or alkylaminohydroquinones. That is, they are hydroquinones, such as hydroquinone or 1,4-naphthohydroquinone, substituted by at least one alkylamino or arylamino group. The hydroquinone nucleus may be substituted, in addition to the alkylamino or arylamino groups, by halogen, alkyl, alkoxy, hydroxy or amino radicals. It is intended that the terms "alkyl," "alkoxy" and "amino" include substituted alkyl, alkoxy and amino radicals. It is intended that the arylamino or alkylamino groups may be further substituted in the aryl or alkyl portions, and they may be derivatives of primary or secondary alkylamino or arylamino compounds.

A preferred group of compounds within the scope of this invention may be characterized by the formula:

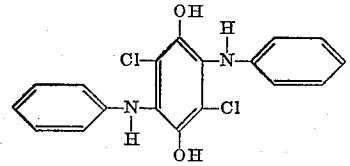



wherein R is an alkylamino or arylamino group, each Y is a hydrogen, hydroxy, halogen, alkyl, amino or alkoxy radical, and *m* is a positive integer less than 3, i.e., *m* is 1 or 2.

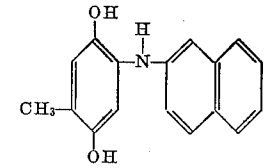
As examples of compounds within the scope of this invention, and particularly within the scope of the above formula, mention may be made of:




2-methyl-5-N-methylanilino-hydroquinone (Ann. 416, 127)




2,5-dichloro-3,6-dianilino-hydroquinone (Beil., 4th ed., 13, 792)




2-(beta-naphthylamino)-5-methyl-hydroquinone

These leuco developing agents may be introduced as the free base but are preferably introduced as a salt, such as the hydrochloride.

The following examples of a photographic use of leuco developing agents in accordance with this invention are given as illustrations only and are not intended to be limiting.

*Example 1*

A photosensitive element is prepared by coating a baryta base with a solution comprising 1 g. of 2-methyl-5-N-methylanilino-hydroquinone hydrochloride in 80 cc. of acetone, 20 cc. of methanol and 1 cc. of ethyl cellosolve. After this coating has dried, a silver-iodobromide emulsion is applied. An image-receiving element is prepared by coating a polyvinyl butyral coated baryta paper with a solution comprising:

| | |
|---|---|
| Acetone ---------- cc-- | 80 |
| "Vinylite MA–28–18" (trade name of Carbide and Carbon Chemical Co., Bakelite Div., for partially hydrolyzed polyvinyl acetate) ---------- g-- | 20 |

The photosensitive element is exposed and brought into superposed relationship with the image-receiving element as a liquid processing composition comprising:

| | |
|---|---|
| Water ---------- cc-- | 100 |
| Sodium carboxymethyl cellulose ---------- g-- | 3 |
| Diethylamine ---------- do---- | 5 |

is spread between said elements. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a yellowish pink, positive image of the photographed subject.

*Example 2*

A photosensitive element is prepared as described in Example 1, using 2 g. of 2-(beta-naphthylamino)-5-methyl-hydroquinone. The image-receiving element is prepared by coating a baryta paper with a 6% aqueous polyvinyl alcohol solution. The liquid processing composition comprises:

| | |
|---|---|
| Water ---------- cc-- | 100 |
| Sodium carboxymethyl cellulose ---------- g-- | 3 |
| Diethylamine ---------- do---- | 10 |
| Metol (p-methylamino phenol) ---------- do---- | 0.2 |

The photosensitive element is exposed and the liquid processing composition applied as it is brought into superposed relationship with the image-receiving element. After an imbition period of approximately one minute, the image-receiving element is separated and contains a positive, brown image of the photographed subject.

2,5-dichloro-3,6-dianilino-hydroquinone may be used to obtain a greenish-yellow image.

It will be noted that the liquid processing composition may, and in Example 2 does, contain a conventional black-and-white developing agent, such as Metol. This conventional developing agent serves to accelerate and possibly initiate the action of the leuco developing agent.

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 either a colored positive 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 materials 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 elements 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 photographic products and processes disclosed and claimed in the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954, now U.S. Patent No. 2,968,554, issued January 17, 1961.

Although British Patent 498,869 states that alkylated or arylated amino-hydroquinones are capable of developing exposed silver halide, the patentee dismisses these compounds as of no value. It was unobvious, therefore, that these developing agents would be useful in diffusion transfer processes.

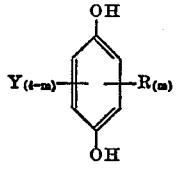
In the preceding portion of the specification, the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

This application is a continuation-in-part of our copending application, Serial No. 473,456, filed December 6, 1954 (now abandoned).

Since certain changes may be made in the above products, compositions and processes 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. In a process of forming photographic images in color, the steps which comprises developing a latent image contained in an exposed silver halide emulsion with an aqueous alkaline solution containing a leuco developing agent of the formula:




wherein R is a radical selected from the group consisting of alkylamino and arylamino radicals, each Y is a radical selected from the group consisting of hydrogen, hydroxyl, halogen, alkyl, amino, and alkoxy radicals, and *m* is an integer from 1 to 2, inclusive, to thereby provide an imagewise distribution of unoxidized leuco developing agent, transferring at least a portion of said distribution of unoxidized leuco developing agent by imbibition from said emulsion to an image-receiving layer in superposed relationship with said emulsion, and oxidizing said diffused, transferred, unoxidized leuco developing agent to impart to said image-receiving layer a reversed positive dye image of the developed image.



2. The process as defined in claim 1 wherein said leuco developing agent is 2-methyl-5-N-methylanilinohydroquinone.

3. The process as defined in claim 1 wherein said leuco developing agent is 2,5-dichloro-3,6-dianilinohydroquinone.

4. The process as defined in claim 1 wherein said leuco developing agent is 2-(beta-naphthylamino)-5-methylhydroquinone.

5. The process as defined in claim 1 wherein said leuco developing agent is disposed, prior to exposure, in a photosensitive element comprising said exposed silver halide emulsion, and said solution containing said leuco developing agent is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said leuco developing agent.

6. The process as defined in claim 5 wherein said liquid is introduced by being spread in a substantially uniform layer between said photosensitive element and an image-receiving element including said image-receiving layer as said elements are brought into superposed relationship.

7. The process as defined in claim 6 wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving element.

8. The process as defined in claim 6 wherein said leuco developing agent is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

9. The process as defined in claim 1 wherein said diffused, transferred, unoxidized leuco developing agent is oxidized by exposure to air.

10. The process as defined in claim 1 wherein said diffused, transferred, unoxidized leuco developing agent is oxidized by an oxidizing agent incorporated in said image-receiving layer.

11. The process as defined in claim 1 wherein said developing is effected in the presence of an accelerating developing agent.

12. The process as defined in claim 1 wherein said accelerating developing agent is p-methylaminophenol.

**References Cited in the file of this patent**

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2,698,244 Land ---------- Dec. 28, 1954

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498,869 Great Britain ---------- Jan. 10, 1939

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