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3,065,074

1,4-BENZOQUINONE OXIDIZING AGENTS FOR COLOR TRANSFER PROCESSES

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This invention relates to photography and more particularly to novel photographic products and processes.

One object of this invention is to provide novel image-receiving elements containing benzoquinone and substituted benzoquinone oxidizing agents for use in diffusion transfer color processes.

Another object is to provide novel processes utilizing said benzoquinone oxidizing agents in diffusion transfer color processes.

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

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product 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.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The present invention is related to diffusion transfer color processes of the type wherein, concurrent with and under the control of the development of a latent silver halide image, in a photosensitive element, a positive image-wise distribution of mobile color-providing materials is formed and transferred to a superposed image-receiving layer to produce a positive dye image thereon.

This invention is more particularly related to those diffusion transfer color processes wherein color-providing developing agents (i.e., developing agents which, upon oxidation, are dyes or are capable of coupling to form dyes) are used to develop a latent image, and the unreacted color-providing developer is transferred to a superposed image-receiving element and utilized to form the positive dye image. As examples of such processes, mention may be made of the processes disclosed in U.S. Letters Patent Nos. 2,559,643 and 2,647,049 to Edwin H. Land wherein the color-providing developing agents used are color developers, and the processes disclosed in the copending application of Howard G. Rogers, Serial No. 464,175, filed October 22, 1954, now abandoned, wherein the color-providing developing agents used are leuco indophenols.

In processes such as disclosed in the above-mentioned patents of Edwin H. Land, a latent silver halide image in a photosensitive element is developed with a color developer. The color developers used may be of the primary or secondary type, i.e., when oxidized they may couple with themselves or with a color coupler to form the dye. As the development proceeds, the color developer reduces the exposed silver to metallic silver, and the portions of the color developer which are oxidized as a result of the development couple with themselves or with a color coupler to form a substantially immobile dye. The unreacted color developer takes on a positive imagewise distribution and is transferred and imbibed on a superposed image-receiving element where it is oxidized and caused to couple to form the positive dye image. The processes are preferably carried out by disposing the color developer and the color coupler (if one is used) in the photosensitive element prior to exposure and, during processing, solubilizing them therefrom with an aqueous alkaline processing

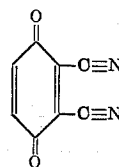
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solution which is spread between the superposed photosensitive and image-receiving elements.

In the processes disclosed in the copending application of Howard G. Rogers, leuco indophenol developing agents are used in place of the color developer and color coupler. The processes proceed substantially as in the color coupler processes except that the positive image is produced by oxidizing the imagewise distribution of unreacted leuco indophenol which is transferred to the image-receiving element during the operation.

In processes such as described above, two methods are proposed for carrying out the required oxidation in the image-receiving element. The first method comprises oxidizing, after stripping the image-receiving element from the photosensitive element, by allowing aerial oxidation to take place or by swabbing with an oxidizing agent. The second method consists of incorporating oxidizing agents, such as peroxides, perborates, perchlorates, permanganates, persulfates, dichromates, polyvalent metals in higher valent form, and benzoyl peroxide, in the image-receiving element, so that oxidation occurs during imbibition. The first method, although effective, leaves much to be desired in that considerable time may have to elapse before the dye image is formed. The second method produces the dye images much more rapidly, but it is found wanting in that the oxidizing agents in turn may act on the dyes of the completed image to cause bleaching or discoloration.

It has been discovered that by using unsubstituted and substituted 1,4-benzoquinones as the oxidizing agents in the image-receiving elements, dye images of good quality are rapidly produced and further oxidation of the resulting dyes by the oxidizing agent is substantially eliminated. Benzoquinones which are substituted by at least one electronegative group are particularly preferred for carrying out the processes of this invention in that the corresponding hydroquinonyl compounds, which are produced as a result of the oxidation, are weak silver halide developing agents and thus have less tendency to interfere with the diffusion transfer processes if they happen to migrate to the photosensitive element during imbibition. In this respect 2,3-dicyano-1,4-benzoquinone of the structure



hydroquinonyl compound is not a developing agent and will not interfere with the diffusion transfer processes if it migrates to the photosensitive element. As examples of electronegative groups which may be substituted on the benzoquinone radicals, mention may be made of carboxyl, sulfo, nitro, cyano, aldo and keto groups. A further class of benzoquinones which are particularly useful in carrying out the processes of this invention are those which are substituted by an alkyl chain containing at least four carbon atoms. Such benzoquinones, because of the alkyl chain, are less apt to migrate to the photosensitive element and interfere with the development. Another mode of preventing migration, during imbibition, comprises the use of polybenzoquinones, i.e., polymers having benzoquinone substituents, as the oxidizing agent in the image-receiving layer. Such polybenzoquinones may be prepared, for example, by oxidizing polyvinyl hydroquinone.

The image-receiving element in which the benzoquinones are incorporated may be constructed from a sheet of any dye-receptive material as, for example, baryta paper. In a preferred embodiment, the image-receiving

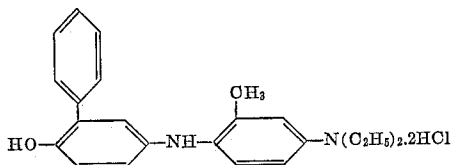
element comprises a film support such as baryta, cellulose nitrate, cellulose acetate, etc., which has been coated with a layer of a dye-receptive polymer. As examples of dye-receptive polymers, useful in preparing the image-receiving elements of this invention, mention may be made of polyvinyl alcohols, polyvinyl pyrrolidones, methyl cellulose and nylons such as Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide). The benzoquinones may be incorporated into the image-receiving element by dissolving them in the coating solution and applying them therewith or by dissolving them in a separate solution and imbibing them, as by swabbing, on the surface adapted to receive the dye image. A further mode of incorporating the benzoquinones in the image-receiving layer comprises dissolving the benzoquinones in a high boiling, organic, water-immiscible solvent, which is also a solvent for the color-providing substances, and emulsifying the hydrophobic solution in an aqueous solution of a water-soluble, dye-receptive material, e.g., polyvinyl alcohol. Such a mode has the advantage of providing a solvent medium in the image-receiving layer in which the subsequent oxidation may take place.

The following nonlimiting example illustrates the preparation and use of a novel image-receiving element of this invention:

Example

An image-receiving element is prepared by coating a cellulose acetate-coated baryta paper with an ethanol solution comprising 4% Nylon Type F8 and 0.025% 2,3-dicyano-1,4-benzoquinone.

A photosensitive element for use with the above image-receiving element is prepared by coating a gelatin-coated film base with an acetone-methanol solution (1 to 4 by volume) comprising 4% cellulose acetate hydrogen phthalate and 0.5% of a leuco indophenol of the formula:



drying the coating and applying thereto a silver indobromide emulsion.

In carrying out the process, the photosensitive element is exposed and an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose.....	4.5
Sodium hydroxide.....	1.5
1-phenyl-3-pyrazolidone	0.2
6-nitrobenzimidazole	0.16

is spread between said photosensitive element and the image-receiving element as said elements are brought into superposed relationship. After an imbibition period of approximately one minute the image-receiving element is separated and contains a cyan positive image.

The above image has better color density than a similar image produced by means of aerial oxidation, and exhibits substantially no discoloration due to oxidation of the resulting dye.

It should be noted that other materials useful in the process, such as dye mordants, ultraviolet absorbers, acids, etc., may be incorporated into the image-receiving element along with the benzoquinones.

It should also be noted that the use of novel image-receiving elements of this invention is in no way limited to diffusion transfer color processes wherein an oxidation reaction is necessary in order to produce the dye image, for they are equally well adaptable to other diffusion transfer color processes such, for example, as the processes disclosed in the copending application of Howard G. Rogers,

Serial No. 748,421, filed July 14, 1958, now U.S. Patent No. 2,983,606, issued May 9, 1961, which is a continuation-in-part of copending application Serial No. 415,073, filed March 9, 1954, now abandoned, wherein dye developers (i.e., dyes which contain, in the same molecule, a silver halide developing function and the chromophoric system of a dye) are used to form color transfer images. In such processes, an exposed photosensitive element is developed in the presence of a dye developer. As the development proceeds, the dye developer in the exposed areas is oxidized as a result of the development and is substantially immobilized. The unreacted dye developer, in unexposed areas, is transferred to a superposed image-receiving element to form a positive image thereon. In the dye developers used in such processes, the silver halide developing function is preferably supplied by a benzenoid silver halide developing radical which may or may not be conjugated with the chromophoric system. When the benzenoid silver halide developing radical is conjugated with the chromophoric system, the image-receiving elements of this invention may be used both to mordant the transferred dye developer and to bring about a bathochromic shift. When the benzenoid developing radical is not conjugated with the chromophoric system, the image-receiving elements of this invention may be used to mordant the transferred dye developers by oxidizing it to its less soluble form.

While in the preferred embodiment the benzoquinones utilized as oxidizing agents are incorporated in the image-receiving layer, it is also possible to utilize them by means of a solution which is swabbed or otherwise applied to the stripped image-receiving layer.

The percentages set forth herein are percentages by weight, unless otherwise indicated.

Another mode of oxidizing the color-providing substances upon their transfer to the image-receiving layer comprises the use of tetrazolium compounds as the oxidizing agents. Such compounds, because of the fact that they are generally colorless in the oxidized state and colored in the reduced state, can be used to increase the density of the transfer image and are especially useful in this respect in monochrome processes.

Since certain changes may be made in the above product and process 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 wherein a latent image contained in an exposed silver halide emulsion is developed with an aqueous alkaline solution comprising a color-providing developing agent to thereby provide an imagewise distribution of unoxidized color-providing developing agent in unexposed areas, said color-providing developing agent being selected from the group consisting of color developers, leuco indophenol silver halide developers, and dye developers, said leuco indophenol silver halide developers being compounds which are both leuco indophenol dyes and silver halide developers and said dye developers being compounds which are both dyes and silver halide developing agents, and wherein at least a portion of said distribution of unoxidized color-providing developing agents is transferred, by imbibition, from said emulsion to an image-receiving layer, in superposed relationship with said emulsion, and the transferred color-providing developing agent is oxidized to partake in the formation of the dye image; the step characterized by the feature that a compound selected from the group consisting of 1,4-benzoquinone and carboxy-, sulfo-, nitro-, cyano-, aldo-, keto-, and alkyl-substituted 1,4-benzoquinone is used as the oxidizing agent.

2. A process as defined in claim 1 wherein said oxidizing agent is present in said image-receiving layer during imbibition.

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3. A process as defined in claim 1 wherein said oxidizing agent is 2,3-dicyano-1,4-benzoquinone.

4. A process as defined in claim 1 wherein said color-providing developing agent is a color developer.

5. A process as defined in claim 1 wherein said color-providing developing agent is a leuco indophenol silver halide developer.

6. A process as defined in claim 1 wherein said color-providing developing agent is a dye developer.

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