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PHOTOGRAPHIC PRODUCTS, COMPOSITIONS, AND PROCESSES

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

This application is in part a continuation of our copending application, Serial No. 478,192, filed December 28, 1954.

It is one object of the present invention to provide novel processes and compositions for the development of silver halide emulsions, in which colored developing agents are used to develop a latent image.

Another object is to provide novel processes and compositions for the development of silver halide emulsions, in which the novel developing agent is capable of developing a latent image and imparting a reversed or positive colored image of said latent image to a superposed image-receiving material.

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 and which possess the ability to function both as a dye and as a photographic developing agent. These compounds may therefore be referred to as dye developers.

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.

The copending application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958 (as a continuation-in-part of Serial No. 415,073, filed March 9, 1954), discloses examples of such diffusion transfer reversal processes wherein a photographic negative material, such as a photographic element comprising an exposed silver halide emulsion layer containing a latent image, is processed to impart to an 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 emulsion layer into superposed relationship with an appropriate image-receiving layer. The processing composition may be applied by rupturing

a container holding said composition, and spreading the released processing composition over the areas to be processed, in accordance with techniques disclosed in the herein mentioned patents and patent applications.

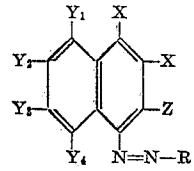
In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. It is also within the scope of this invention to apply the liquid processing composition 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 liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the latent image is developed, the oxidation product of the dye developer is immobilized or precipitated as a function of development of exposed areas, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solutions. It may also be due, in part, to a tanning effect on the emulsion by the oxidized developing agent, and to a reduction in the solvent power of the processing composition as a result of the local exhaustion of alkali during development. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving element, said transfer substantially excluding oxidized dye developer. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide a reversed or positive, colored image of the negative image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. 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 dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the emulsion is exposed and preferably also adapted to be most distant from the image-receiving element when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred

embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the colored dye developer. In this preferred embodiment, the layer of dye developer may be applied by using a coating solution containing about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition.

The liquid processing composition above referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain a minor amount of a conventional developing agent. 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 inert to an alkali solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

The dye developers which may be used to accomplish the objects of this invention are arylazonaphthalene compounds which possess a silver halide developing function on the naphthalene nucleus supplied, at least in part, by amino groups. These compounds may be represented by the formula:



wherein one X is amino and the other X is selected from the group consisting of hydroxyl and amino radicals, R is selected from the group consisting of unsubstituted and substituted aryl groups, Y_1, Y_2, Y_3 and Y_4 are selected from the group consisting of hydrogen, hydroxyl, amino, alkyl, carboxyl, sulfo, halogen, aryl, alkoxy and aryloxy radicals, Z is selected from the group consisting of hydrogen, hydroxyl, amino, alkyl, carboxyl, sulfo, halogen, aryl, alkoxy and aryloxy radicals where one X is hydroxyl, and from the group consisting of hydrogen, hydroxyl, amino, alkyl, halogen, aryl, alkoxy and aryloxy radicals where both X's are amino. R may be substituted by halogen, alkyl, aryl, amino, nitro, sulfo, hydroxyl, alkylamido, arylamido, carboxamido, etc. The expression "amino" is intended to include "alkylamino."

The dye developers of this invention may be prepared by coupling a diazonium derivative of the aryl group R with the appropriate amino-substituted naphthalene compound.

As examples of dye developers within the scope of this invention, mention may be made of:

1-amino-4-phenylazo-2-naphthol
1-amino-4-(p-sulfophenylazo)-2-naphthol
1-amino-4-(p-nitrophenylazo)-2-naphthol
2-amino-4-(m-nitrophenylazo)-1-naphthol

The following examples of a photographic use of the dye developers of this invention are given as illustrations only.

Example 1

A photosensitive element is prepared by applying two coats of a solution of 1 g. of 1-amino-4-(p-sulfophenylazo)-2-naphthol in a solution comprising 4 g. of cellulose acetate hydrogen phthalate, 80 cc. of acetone, 20 cc. of methanol and 1 cc. of ethyl Cellosolve to a baryta paper base. After these coats have dried, a silver iodobromide emulsion is applied. The photosensitive emulsion is exposed and a liquid processing composition comprising:

Water	cc.	100
Sodium carboxymethyl cellulose	g.	3
Diethylamine	g.	10

is applied to the exposed photosensitive element as the latter is brought into superposed relationship with an image-receiving element. The image-receiving element is prepared by coating a polyvinyl butyral-coated baryta base with a solution comprising:

Vinylite MA–28–18 (trade name of Bakelite Division, Carbide and Carbon Chemicals Co., for partially hydrolyzed polyvinyl acetate)	g.	20
Acetone	cc.	80

After an imbibition period of approximately one minute, the image-receiving element is separated and contains a yellow positive image of the photographed subject.

Example 2

A photosensitive element is prepared by coating a baryta base with a solution of 1 g. of 1-amino-4-phenylazo-2-naphthol in a solution comprising 4 g. of cellulose acetate hydrogen phthalate, 80 cc. of acetone, 20 cc. of methanol and 1 cc. of ethyl Cellosolve. A silver iodobromide emulsion is then applied after which the photosensitive element is exposed. A liquid processing composition comprising:

Water	cc.	100
Sodium carboxymethyl cellulose	g.	4
Sodium hydroxide	g.	1.5
Phenyl ethyl alcohol	g.	1.5

is applied to the exposed photosensitive element as it is brought into superposed relationship with an image-receiving element. The latter element is prepared by coating a baryta base with a 6% aqueous polyvinyl alcohol solution. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a salmon pink positive image of the photographed image.

It should be noted that certain dye developers within the scope of this invention may be subject to color changes as a result of pH changes in the portion of the image-receiving element to which they are diffused. Thus, the color of 1-amino-4-(p-sulfophenylazo)-2-naphthol remains yellow when the surface of the image-receiving element is made alkaline, whereas the color of 1-amino-4-phenylazo-2-naphthol is affected by pH changes. Since the dye developer is rendered effective by solution in an aqueous alkaline liquid processing composition, it accordingly is necessary to assure that the environment in which the transferred and unreacted dye developer is deposited has, or is capable of attaining, the requisite pH value affording the desired color to the diffused dye developer. 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 transferred and unreacted dye developer 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 noted that the liquid processing composition may contain an auxiliary or accelerating silver halide developing agent, such as Metol (p-N-methylaminophenol),

Amidol (2,4-diaminophenol), or a 3-pyrazolidone, such as 1-phenyl-3-pyrazolidone (commercially available under the trade name of Phenidone). The auxiliary developer serves to accelerate and possibly initiate the action of the dye developer. A portion of the dye developer may be oxidized by an energy-transfer reaction with oxidized auxiliary developer.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black-and-white, monochromatic or toned prints or negatives. By way of example, a developer composition suitable for such use may comprise an aqueous solution of approximately 1 to 2% of the dye developer, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye developer is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye developer is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

It should be noted that the dye developers of this invention are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction between a "color former" or "coupler" and the oxidized developing agent, as well as so-called auto-coupling processes in which color is obtained by a reaction of the oxidized developing agent with unoxidized 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 an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Patent No. 2,647,049 to Edwin H. Land.

The inventive concepts herein set forth are also adaptable for the formation of colored images in accordance with the photographic products and processes described 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, and also those set forth in the copending application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956.

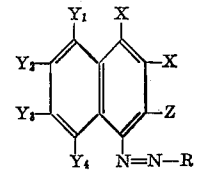
In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

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 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 containing a dye developer of the formula:



wherein one X is amino and the other X is selected from the group consisting of hydroxyl and amino radicals, R is selected from the group consisting of unsubstituted and substituted aryl groups, Y_1, Y_2, Y_3, and Y_4 are selected from the group consisting of hydrogen, hydroxyl, amino, alkyl, carboxyl, sulfo, halogen, aryl, alkoxy and aryloxy radicals, Z is selected from the group consisting of hydrogen, hydroxyl, amino, alkyl, carboxyl, sulfo, halogen, aryl, alkoxy and aryloxy radicals where one X is hydroxyl, and from the group consisting of hydrogen, hydroxyl, amino, alkyl, halogen, aryl, alkoxy and aryloxy radicals where both X's are amino, to provide in said emulsion a predetermined distribution of unoxidized dye developer, and transferring at least part of said distribution of unoxidized dye developer by imbibition from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart to said image-receiving element a reversed, positive dye image of the developed image.

2. The process as defined in claim 1, wherein said dye developer is 1-amino-4-phenylazo-2-naphthol.

3. The process as defined in claim 1, wherein said dye developer is 1-amino-4-(p-sulfophenylazo)-2-naphthol.

4. The process as defined in claim 1, wherein said dye developer is 1-amino-4-(p-nitrophenylazo)-2-naphthol.

5. The process as defined in claim 1, wherein said dye developer is disposed, prior to exposure, in a photosensitive element containing said emulsion, and the solution containing said dye developer is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said dye developer.

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 comprising 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 1, wherein said dye developer 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 development is effected in the presence of a silver halide developer.

10. The process as defined in claim 9, wherein said silver halide developer is p-N-methyl-aminophenol.

11. The process as defined in claim 9, wherein said silver halide developer is 1-phenyl-3-pyrazolidone.

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