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PHOTOGRAPHIC PROCESSES

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This invention relates to photography and more particularly to 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 reversed 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 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 compositions processing 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 1-phenyl-3-pyrazolidone, hereinafter described, which I have discovered possesses the ability to function as a photographic developing agent and to produce colored products upon oxidation.

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 1-phenyl-3-pyrazolidone, 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 said developer substantially uniformly distributed therein. As the developer 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 developer 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 developer. The unoxidized developer retains its solubility in the liquid processing composition, thereby providing an imagewise distribution of unoxidized developer, at least part of which is transferred, by imbibition, to a superposed image-receiving element, said transfer substantially excluding silver or oxidized developer. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized developer without appreciably disturbing its imagewise distribution. The unoxidized developer 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 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 1-phenyl-3-pyrazolidone 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, said developer becomes solubilized by the liquid processing composition as it permeates the element. In a preferred embodiment, the coating or layer of the developer 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 developer behind the emulsion layer has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action if the developer is colored. If the developer is colorless, it may be incorporated in the silver halide emulsion without adverse light-filtering effect. Where the developer 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 developer. Similar concentrations may be used if the developer 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 developer 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 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 following example illustrates the use of 1-phenyl-3-pyrazolidone in accordance with this invention.

Example

A photosensitive element is prepared by coating a gelatin coated-film base with a solution comprising:

Acetone	cc.	80
Methanol	cc.	20
Cellulose acetate hydrogen phthalate	g.	4
1-phenyl-3-pyrazolidone	g.	4

When this coating has dried, a silver-iodobromide emulsion is applied. The photosensitive element thus prepared is exposed and then brought into superposed relationship with an image-receiving element as a liquid processing composition comprising:

Water	cc.	100
Sodium carboxymethyl cellulose	g.	4.5
Sodium hydroxide	g.	2.0

is spread between said elements. The image-receiving element comprises a cellulose acetate coated baryta paper which is coated with a 6% aqueous polyvinyl alcohol solution. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive image of the photographed subject.

The 1-phenyl-3-pyrazolidone herein contemplated has been used in conventional photographic processes; note U. S. Patent No. 2,289,367, issued to John D. Kendall on July 14, 1942. The photographic art has not, however, recognized the color-producing properties of this compound. Indeed, it has been stated by Thomas T. Hill, Photographic Engineering, vol. 5, No. 4, pp. 239–240, that the oxidation products of 1-phenyl-3-pyrazolidone are colorless. Thus, it was quite unexpected to discover that this compound may be effectively employed to produce a colored, positive image in a diffusion transfer-reversal process.

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. In a preferred embodiment, the unoxidized 1-phenyl-3-pyrazolidone is transferred to a polyvinyl alcohol surface. The inventive concepts herein set forth also 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 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 the previously mentioned 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 Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, 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.

Since certain changes may be made in the above 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 of 1-phenyl-3-pyrazolidone to provide in said emulsion a predetermined distribution of unoxidized 1-phenyl-3-pyrazolidone, transferring at least part of said distribution of unoxidized 1-phenyl-3-pyrazolidone by imbibition from said emulsion to an image-receiving layer consisting essentially of polyvinyl alcohol in superposed relationship with said emulsion, and oxidizing at least part of said transferred unoxidized 1-phenyl-3-pyrazolidone to impart to said image-receiving layer a reversed, positive color image of the developed image.

2. The process as defined in claim 1 wherein said 1-phenyl-3-pyrazolidone is disposed, prior to exposure, in a photosensitive element containing said emulsion, and the solution containing said 1-phenyl-3-pyrazolidone is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said 1-phenyl-3-pyrazolidone.

3. The process as defined in claim 2 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.

4. The process as defined in claim 3 wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said elements.

5. The process as defined in claim 1 wherein said 1-phenyl-3-pyrazolidone is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

6. The process as defined in claim 1 wherein said transferred, unoxidized 1-phenyl-3-pyrazolidone is oxidized by aerial oxidation.

7. The process as defined in claim 1 wherein said transferred, unoxidized 1-phenyl-3-pyrazolidone is oxidized by an oxidizing agent disposed in said image-receiving element.

8. A process of forming a photographic image in color comprising exposing a photosensitive element comprising a silver halide emulsion and a layer containing 1-phenyl-3-pyrazolidone behind said emulsion, applying an aqueous alkaline solution to the exposed silver halide emulsion and developing the latent image formed in said silver halide emulsion to provide a predetermined distribution of unoxidized 1-phenyl-3-pyrazolidone, transferring at least part of said distribution of unoxidized 1-phenyl-3-pyrazolidone by imbibition from said emulsion to an image-receiving layer consisting essentially of polyvinyl alcohol in superposed relationship with said emulsion, and oxidizing at least part of said transferred, unoxidized

1-phenyl-3-pyrazolidone to impart to said image-receiving layer a reversed, positive color image of the developed latent image.

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