# United States Patent

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## [54] PHOTOGRAPHIC REVERSAL COLOR PROCESS

**7 Claims, No Drawings**


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[50] **Field of Search** ..... 96/22, 55, 66, 66 HD



[56] **References Cited**

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**ABSTRACT:** A reversal color development process in photography is carried out at elevated temperatures using a first black-and-white silver halide developing solution at pH of about 9.1 to 9.6 and containing hydroquinone and an amount of 3-pyrazolidone silver halide developing agent sufficient to inhibit fog on development of aged emulsion layers. This minimizes the density losses obtained with aged color films compared to fresh color films.

# PHOTOGRAPHIC REVERSAL COLOR PROCESS

This invention relates to color photography and more particularly to photographic color development processes carried out at elevated temperatures.

Well-known processes of color photography utilize sensitive elements having differently sensitized silver halide emulsion layers. The elements are processed in a series of operations including development, fixation and washing. These operations have long been carried out at temperatures of about 70° to 80° F. More recently, elevated processing temperatures of about 100° to 125° F. have been used to reduce the processing time. In the known reversal color process in which the exposed emulsion layers are first developed with a black-and-white developer followed by a reversal color developer, when processing is carried out at the higher temperatures of about 125° F., it is found that the freshly coated emulsions yield dye images having the desired density and contrast. However, when the same emulsions have been aged and are processed at about 125° F., due to fog in the emulsions caused by aging, the dye images obtained have lower density than the dye images obtained from the freshly coated emulsions. As a result, the black images are lacking in density, the colored images are lacking in saturation and detail is lacking in areas of low exposure. This problem with aged color products does not appear to exist when a lower processing temperature of about 100° F. is used. The seriousness of the problem will be appreciated when it is understood that in the commercial color processing, both fresh and aged color emulsions must be processed through the same solutions and the colored images, as nearly as possible, should have the same sensitometric properties regardless of the age of the emulsions.

We have discovered that the mentioned reversal color processes can be carried out at elevated temperatures of about 100° –125° F. or higher to obtain substantially identical color images in either freshly coated or aged emulsion layers.

It was found that if the black-and-white developing solution contains both hydroquinone and a 3-pyrazolidone silver halide developing agent, the latter being present in a relatively high concentration, and the solution has a relatively low pH, development fog on the aged emulsions is effectively inhibited and dye images of comparable sensitometric characteristics are obtainable from both fresh and aged color products. That is, the 3-pyrazolidone developing agent must be used at a higher concentration than usually employed for processing at lower temperatures of about 70° to 100° F. Also, the pH of the developer solution must be substantially lower than normally used when processing at the lower temperatures.

Our invention arose in the following manner. Previously, developer solutions containing mixtures of silver halide developing agents such as hydroquinone and Elon or hydroquinone and a 3-pyrazolidone have been used for the black-and-white developer for color reversal processes. Customarily, when processing representative color products by reversal at about 70° to 100° F., the hydroquinone-3-pyrazolidone developers contain about 0.3 to 0.4 grams of the 3-pyrazolidone per liter solution at a pH of about 10.0. However, as indicated above, when processing aged film under these conditions of developer concentration and pH at elevated temperatures of about 125° F., the mentioned serious losses of image density are obtained. Unexpectedly, we discovered that by increasing the concentration of the 3-pyrazolidone to about 0.5 to 1.0 gram per liter (in the case of 1-phenyl-3-pyrazolidone) or to about 1 to 2.5 grams per liter of less active 3-pyrazolidones, the Dmax losses of some, but not all, of the aged emulsion layers could be prevented. For example, in a color product having superposed red, green and blue-sensitive emulsion layers containing couplers for color development of cyan, magenta and yellow dye images, respectively, in the layers, the increase in 3-pyrazolidone concentration only prevents Dmax losses in the cyan and magenta layers, whereas the outermost yellow layer still sustains the Dmax loss. Unexpectedly, we further discovered that when the pH of the hydroquinone-3-pyrazolidone developer (having



increased 3-pyrazolidone concentration) was reduced from 10.0 to about 9.1 to 9.6, the Dmax loss of even the yellow emulsion layer was prevented. Variation of the concentration of hydroquinone in the developer does not give the same result as will be seen from the data below, and at least about 1.5 grams per liter is needed. A further unexpected feature of our investigation resides in the finding that developer solutions, such as hydroquinone-Elon (monomethyl-*p*-aminophenol sulfate) developers, could not be modified in this manner to reduce the Dmax losses of the aged color products. That is, as shown by data in the examples below, even a range of concentration of from about 1.3 to 6.0 grams of Elon per liter does not prevent the Dmax losses of the emulsion layers.

For these reasons, our invention includes using as the black-and-white developer of reversal color processes, an alkaline developer solution of pH of about 9.1 to 9.6 containing at least about 1.5 grams hydroquinone per liter and an amount of a 3-pyrazolidone developing agent sufficient to inhibit the development of fog on the aged emulsions and, accordingly, prevent Dmax losses in these emulsions. Thus, comparable development of both fresh and aged emulsion layers is obtained using this developer. When using 1-phenyl-3-pyrazolidone, at least about 0.5 gram, preferably 0.5 to 1.0 grams, per liter, are useful. When using other less active 3-pyrazolidone developing agents, such as the 1-phenyl-3-pyrazolidone substituted by lower alkyl in the 4-position of the nucleus, at least 1.0 gram, preferably 1 to 2.5 grams, per liter is useful as can be seen from the data below.

The 3-pyrazolidones which are used in the developer solution include those substituted in the 1-position by a monocyclic aryl group of the benzene series including phenyl and substituted phenyl such as *p*-tolyl, *p*-chlorophenyl, etc., or substituted in the 1-position by cycloalkyl such as cyclohexyl. A very useful compound of this class is 1-phenyl-3-pyrazolidone.

In addition to this substitution in the 1-position, the pyrazolidone nucleus can be substituted in the 4-position particularly by lower alkyl and substituted lower alkyl such as methyl and hydroxymethyl. Representative compounds of this class are 1-phenyl-4, 4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidine,1-phenyl-4-hydroxymethyl-3-pyrazolidone and 1-phenyl-4,4-di(hydroxymethyl)-3-pyrazolidone. As mentioned and shown by data below, these 4-substituted 3-pyrazolidone compounds are used in the developer solution in concentrations of greater than about 1.0 gram per liter, preferably 1.0 to 2.5 grams per liter.

In a typical reversal color process a multilayer color film is exposed to a colored subject, developed in the above-mentioned black-and-white hydroquinone-3-pyrazolidone developer solution to obtain negative silver images in the region of exposure. According to the invention, by use of this developer either fresh or aged film can be used and processing carried out at, e.g., 125° F. The unexposed silver halide is then exposed or treated with a bath containing a chemical nucleating agent such as an amine borane. In case color-forming couplers are present in the emulsion layers, a conventional color developing solution containing a phenylenediamine type developing agent is employed to form subtractively colored positive dye images in the layers. In subsequent steps the film is bleached, fixed and washed as usual for removal of silver and residual silver halide from the layers. In case the color film does not contain coupler compounds, after use of the hydroquinone-3-pyrazolidone developer, selective reversal color development is carried out in the usual manner using *p*-phenylenediamine developers containing the usual color couplers.

Particularly useful color products for reversal processing according to the method of our invention comprise a conventional support, such as cellulose esters, paper, glass, polyester film, polyvinyl acetal film, polycarbonate film, etc., having coated thereon at least two silver halide layers which have been sensitized to particular regions of the spectrum. These emulsions have incorporated therein the color-forming com-

ponents or couplers, which combine with the oxidation products of the photographic color developers, to produce the desired color images. For example, a typical color film, useful in practicing our invention comprises a support having coated thereon a red-sensitized photographic silver halide emulsion having incorporated therein a coupler for the cyan image (e.g., a phenolic coupler), a green-sensitized photographic silver halide emulsion having incorporated therein a coupler for the magenta image (e.g. pyrazolone coupler), and a blue-sensitized photographic silver halide emulsion containing a coupler for the yellow image e.g., a coupler containing an open-chain ketomethylene group). The photographic element can also contain conventional interlayers and filter layers, such as a yellow filter layer beneath the blue-sensitized emulsion to prevent exposure by blue light to either the red- or green-sensitized emulsion. Such multilayer materials have been previously described in the prior art, such as U.S. Pat. No. 2,322,027 issued June 15, 1943, and U.S. Pat. No. 2,644,900 issued July 12, 1960. Other arrangements of the sensitive layers are also shown.

The following examples will serve to illustrate our invention.

## EXAMPLE 1

An incorporated coupler multilayer color film is provided comprising red, green and blue sensitive gelatin-silver halide emulsion layers on a support, a yellow filter being coated between the blue- and green-sensitive emulsion layers. The emulsion layers contain reactive methylene and phenolic coupler compounds reactive with *p*-phenylenediamine developing agents to form dyes of color complementary to the sensitivity of the respective layers. The film can be prepared as described in U.S. Pat. No. 2,322,027. The film in sheet or roll form is exposed to a colored subject and processed in a roller transport system such as shown in U.S. Pat. No. 3,025,779 having staggered driven rollers which advance the film through a series of tanks at 125° F. and a drying chamber as follows: Prehardening—37 seconds

Acidic aldehydic solution prepared from dimethoxytetrahydrofuran as described in Munro, U.S. Pat. No. 3,345,173. Neutralizing —25 seconds

Acidic hydroxylamine solution as described in Blackmer U.S. Pat. No. 3,168,400. Negative Developer

After washing the neutralized film, the following developer solution is used for 60 seconds.

| | |
|---|---|
| Water | 800 ml. |
| Quadrafos | 2.0 g. |
| Sodium sulfite, anhydrous | 44.0 g. |
| Phenidone | 0.6 g. |
| Hydroquinone | 5.5 g. |
| Sodium thiocyanate | 1.38 g. |
| Sodium bromide, anydrous | 1.30 g. |
| Potassium iodide (0.1% solution in water | 13.0 ml. |
| Potassium hydroxide, 45% solution | 8.8 ml. |
| Boric acid | 10.2 g. |
| Water to | 1 liter |
| pH at 80° F. | 9.25±0.05 |

Stop bath —40.5 seconds
Dilute acetic acid.
Wash —40.5 seconds
Color Development —122 seconds

| | |
|---|---|
| Water | 800 ml. |
| Quadrafos | 5.0 g. |
| Benzyl alcohol | 4.5 ml. |
| Sodium sulfite, anydrous | 7.5 g. |
| Trisodium phosphate · 12 $H_2O$ | 36.0 g. |
| Sodium bromide | 0.90 g. |
| Potassium iodide (0.1% solution in water) | 90.0 ml. |
| Sodium hydroxide | 3.25 g. |
| Citrazinic acid | 1.50 g. |
| 4-amino-N-ethyl-N-[β-methanesulfonamidoethyl]-*m*-toluidine sesquisulfate monohydrate | 11.0 g. |
| Ethylenediamine | 3.0 g. |
| Tertiary-butylamine borane | 0.07 g. |
| Water to | 1 liter |
| pH at 80° F. | 11.65±0.10 |

Stop Bath —40.5 seconds
Dilute acetic acid
Wash —81 seconds
Bleach —40.5 seconds
Ferricyanide - bromide
Fix —40.5 seconds

Ammonium thiosulfate Wash —57 seconds Drying —96 seconds, 135° F.

As a result of processing both fresh film, and film aged for one week at 120° F. and 50 percent RH, in the above process, development fog of the aged film is found to be inhibited and there is little loss of Dmax in either the cyan, magenta or yellow scales.

## EXAMPLE 2

The effect of variation of 1-phenyl-3-pyrazolidone concentration and pH of the negative black-and-white developer in the process of example 1 is shown in the following table.

TABLE 1

| Concentration of phenidone, g./l. | pH | $D_{max}$ loss for film aged for one week at 120° F., 50% RH vs. check film aged at −10° F. R | G | B |
|---|---|---|---|---|
| .18 [1] | 9.9 | −.25 | −.22 | −.66 |
| .36 [1] | 9.9 | −.20 | −.16 | −.68 |
| .54 [1] | 9.9 | −.11 | −.06 | −.57 |
| .79 [1] | 9.9 | −.11 | −.07 | −.64 |
| 1.04 [1] | 9.9 | −.07 | −.02 | −.46 |
| .79 | 9.9 | −.24 | −.16 | −.43 |
| .79 | 9.55 | −.17 | −.13 | −.27 |
| .79 | 9.10 | −.14 | −.10 | −.18 |

[1] In these tests no antifoggant was present in the prehardener; in the other tests an antifoggant was in the prehardener.

In view of these and other data, it is considered that acceptable Dmax loss for the aged color film is obtainable if the pH of the developer is about 9.1 to 9.6 and the 1-phenyl-3-pyrazolidone concentration is greater than about 0.5 gram per liter, preferably about 0.5 to 1.0 gram per liter, which concentration range appears adequate to inhibit fog formation on development and, thus, prevent Dmax loss of the color scales.

Additional tests show that concentration of the hydroquinone in the developer is not especially critical, at least about 1.5 grams per liter being needed. Thus, Dmax loss of aged film is not affected when about 3 to 24 grams per liter of hydroquinone is used with 4-methyl-1-phenyl-3-pyrazolidone or when about 5 to 12 grams of hydroquinone is used with 1-phenyl-3-pyrazolidone.

## EXAMPLE 3 —Effect of varying Elon in Elon-Hydroquinone Negative Developer

The process of example 1 carried out except replacing 1-phenyl-3-pyrazolidone by Elon in the concentrations shown below.

| Concentration of Elon, g./l. | pH | $D_{max}$. loss of 120° F., 50% RH aged film vs. fresh fil n emulsion R | G | B |
|---|---|---|---|---|
| 1.3 | 9.9 | −.50 | −.48 | −.67 |
| 2.5 | 9.9 | −.44 | −.37 | −.47 |
| 4.0 | 9.9 | −.46 | −.36 | −.49 |
| 6.0 | 9.9 | −.42 | −.32 | −.47 |
| 1.3 | 10.47 | −.50 | −.46 | −.64 |
| 1.3 | 9.90 | −.45 | −.44 | −.61 |
| 1.3 | 9.48 | −.44 | −.40 | −.50 |
| 1.3 | 9.10 | −.63 | −.65 | −.62 |

From these data it is seen that variation of pH and Elon concentration does not adequately prevent Dmax loss in any of the color scales.

## EXAMPLE 4

The process of example 1 is carried out except using varying concentrations of 4-methyl-1-phenyl-3-pyrazolidone, 1-phenyl 4,4-dimethyl-3pyrazolidone, 4-hydroxymethyl-3-pyrazolidone, or 1-phenyl-4,4-bis(hydroxymethyl)-3-

pyrazolidone in the negative developer and varying pH. As a result, development fog is inhibited and, thus, Dmax loss of film aged one week at 120° F. and 50 percent RH is prevented when using about 1 to 2.5 grams of these developing agents per liter and pH of about 9.1 to 9.6.

## EXAMPLE 5

A multilayer color film having red-, green- and blue- sensitive emulsion layers (free of couplers) is processed by selective reversal using the negative developer of example 1. After stopping development, the film is washed, reexposed through the base to red light and developed with a conventional color developer solution containing a phenolic coupler for the cyan dye image. After washing, the film is reexposed to blue light from the emulsion side and developed as usual in a color developer containing a reactive methylene type coupler which forms the yellow dye image. After washing, the film is treated with a magenta reversal bath containing nucleating agents such as disclosed in U.S. Pat. No. 2,984,567 and 3,246,987, e.g., amine boranes. Thereafter, magenta development is carried out using a color developer containing a pyrazolone coupler for formation of the magenta dye image. The process completed after the usual washing, bleaching, washing and fixing steps have been carried out. As a result, fresh and aged color film have comparable Dmax values in the color scales.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a photographic reversal color process wherein a photographic element comprising at least two superposed gelatin-silver halide emulsion layers sensitive to different regions of the spectrum is exposed to a colored image, silver images are developed in the emulsion layers in the regions of exposure using a first black-and-white silver halide developing solution at elevated temperature, and reversal colored images are developed in the remaining undeveloped regions of the emulsion layers at elevated temperature at least about 100° F., the improvement comprising using as said first developing solution an aqueous alkaline solution having a pH of about 9.1 to 9.6 and containing at least about 1.5 grams hydroquinone per liter and an amount of a 3-pyrazolidone silver halide developing agent sufficient to inhibit fog formation upon development of said emulsion layers in said alkaline solution.

2. In a photographic reversal color process wherein a photographic element comprising at least two superposed gelatin-silver halide emulsion layers sensitive to different regions of the spectrum is exposed to a colored image, silver images are developed in the emulsion layers in the regions of exposure using a first black-and-white silver halide developing solution at elevated temperature, and reversal colored images are developed in the remaining undeveloped regions of the emulsion layers at elevated temperature at least about 100° F., the improvement comprising using as said first developing solution an aqueous alkaline solution having a pH of about 9.1 to 9.6 and containing at least about 1.5 grams hydroquinone per liter and at least about 0.5 of 1-phenyl-3-pyrazolidone per liter or at least about 1.0 gram per liter of a 1-phenyl-3-pyrazolidone substituted in the 4-position of the pyrazolidone nucleus.

3. The process according to claim 1 wherein the emulsion layers of the photographic element contain color-forming coupler compounds reactive with primary aromatic amino silver halide developing agents to produce dye images of color complementary to light sensitivity of the respective layers.

4. The process according to claim 1 wherein the said first developer solution contains about 0.5 to 1.0 gram per liter of 1-phenyl-3-pyrazolidone and about 5 to 12 grams per liter of hydroquinone.

5. The process according to claim 1 wherein the emulsion layers of the photographic element are free of color-forming coupler compounds and reversal color development is carried out by means of color developing solutions containing couplers to produce dye images of colors complementary to the light sensitivity of the emulsion layers.

6. The process according to claim 3 wherein the said first developer solution contains about 1.0 to 2.5 grams per liter of 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4-hydroxymethyl-3-pyrazolidone or 1-phenyl-4,4-bis(hydroxymethyl)-3pyrazolidone and about 1.5 to 24.0 grams per liter of hydroquinone.

7. The process according to claim 3 wherein, prior to the first development step the emulsion layers are prehardened using an acidic aldehydic gelatin hardening solution followed by an aldehyde neutralizing solution.