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RAPID COLOR REVERSAL PHOTOGRAPHIC DEVELOPING PROCESS

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ABSTRACT OF THE DISCLOSURE

A process for developing an exposed color reversal photographic material rapidly which comprises black-and-white developing the color reversal photographic material for shorter than 30 seconds, said material comprising a support having coated thereon at least one silver halide emulsion layer containing a color coupler, said support being (a) a paper having a weight of less than 100 g./m.^{2}, (b) a synthetic resin-coated paper, (c) a resin-impregnated paper having a low water-absorptive property or (d) a resin film, color-developing it for shorter than 60 seconds, and bleach-stabilizing it for shorter than 60 seconds, said processing steps containing no water-washing step.

The present invention relates to a rapid reversal developing process for obtaining color photographic images with color films or color photographic papers in a very short period of time.

A color photographic light-sensitive material to be processed by the process of this invention is produced by applying at least one light-sensitive emulsion layer comprising a silver halide emulsion and a coupler to a support. For instance, such light-sensitive material includes a single-layer color photographic material which gives a colored line image and is used for display, a color photographic material for drawing which has two or three light-sensitive emulsion layers each containing a different coupler and having a different spectrally sensitive region, thus giving three-colored or seven-colored line image, a light-sensitive material for scientific recording such as recording material for an oscillogram, and a light-sensitive material developed for industrial purposes.

A light-sensitive material used for scientific researches such as for oscillogram recording or photographic recording in industrial fields, is required to give images in a short period of time. Also, it is profitable that a photographic light-sensitive material for reproducing drawings can be rapidly processed. For processing such light-sensitive material rapidly, a process in which a positive image is directly obtained by reversal development is more profitable than a conventional process in which a positive image is obtained through a negative light-sensitive material by two image-forming steps. Accordingly, the development of a rapid reversal developing process for color photographic light-sensitive materials has large practical merit and also is profitable not only for industrial purposes, scientific researches, drawings, and audio-visual education but also for general color photographic light-sensitive materials.

However, a color reversal photographic developing process conventionally practiced usually requires a processing time of from 30 minutes to one hour. For instance, even the conventional process of the shortest processing time among the known high-temperature rapid processing requires a processing time of about 20 minutes, and further, it requires a large volume of water for washing, and also the processing steps are complicated. The complication of the conventional developing process is as follows: that is to say, in the conventional reversal color process such steps as a black-and-white development (so-called "primary development"), a color development, a stop, and a bleach or a bleach-fixation are inevitably employed, and it requires not only washings between the steps but also, often, such additional steps as prehardening, post-bath, and salt-bath. Consequently, the conventional color reversal process requires usually more than 10 steps. Therefore, such development is usually conducted in a developing laboratory having well-furnished equipment.

Such requirements of long processing time, the installation costs and techniques for managing processing steps have limited the use of color photographic light-sensitive materials for such uses as requiring a rapid and simple processing, such as the use for drawings, industrial purposes, scientific purposes, displays, etc.

On the other hand, an attempt to obtain images readily and in a short period of time has been made by using a color photographic diffusion transfer process. However, such process is accompanied with the faults that an enlargement is not carried out, that a negative material and an image receiving material must be used, and hence the practical use of the process is restricted by such aspects.

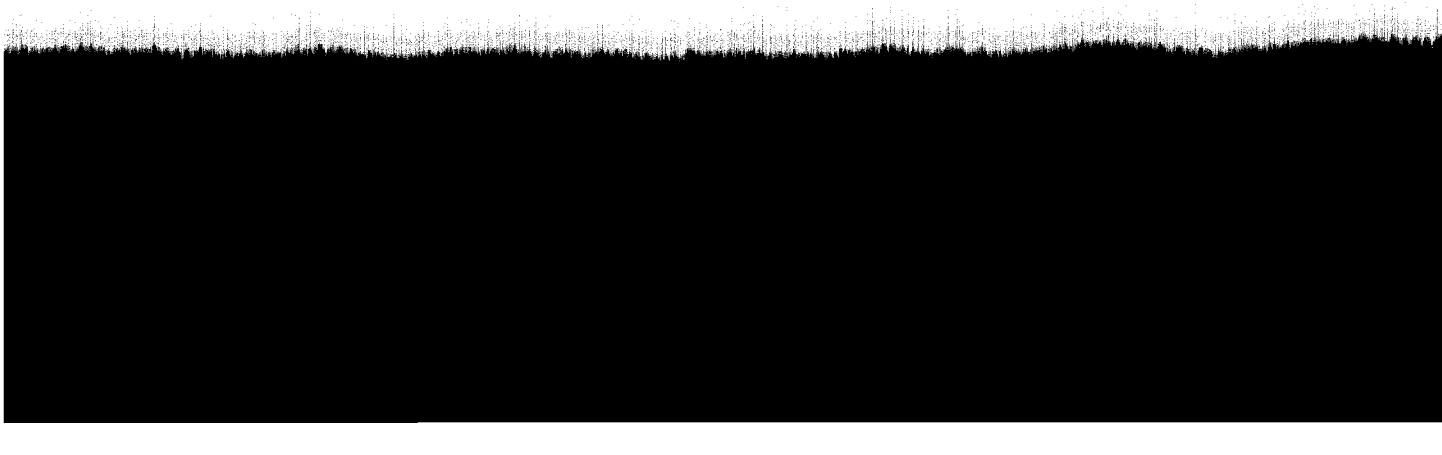
An object of the invention is, therefore, to provide a rapid and simple color reversal photographic developing process for color photographic light-sensitive materials.

For the purpose mentioned above, the inventors have now discovered an economical and practical reversal developing process by which reversal color photographic materials can be processed within three minutes with no washing water or a very small amount of washing water, and the steps of which can be easily controlled.

According to a conventional reversal developing process, it is difficult in various points to shorten the processing time. First of all, since the conventional process includes a large number of steps as mentioned above and there is a limitation for shortening the processing time of each step, the whole process is not satisfactorily shortened in the processing time and even if the process could be shortened, the fault that the process is complicated would not be overcome.

Therefore, for simplifying the steps for the processing, it may be considered to omit the washing steps, but, in such case, the photographic properties of the images will be reduced owing to the contamination of each processing solution during processing and hence such an attempt is not practically employed. Also, an attempt to use a multi-purpose bath, for instance, an attempt to conduct the bleaching and the fixing in one step by combining the bleaching solution and the fixing solution may be considered, but the processing solution thus combined becomes unstable. If a stable composition is employed for such combined system, the processing speed will be reduced.

For conducting readily and rapidly a color reversal photographic process without the accompanying faults, the following improvement is applied in accordance with the present invention. That is to say, for effectively simplifying the process, washing steps must be omitted and also for preventing the degradation of the photographic properties of the images formed in the case of omitting the washing steps, it is necessary to prevent a processing solution from being transferred to the next processing bath carried by the photographic material or carrier therefor. For the purpose, a thin paper having a weight of less than 100 g./m.^{2}, a non-water-absorptive resin-coated paper which is obtained by coating a resin layer on a paper or by impregnating a paper with a resin, or a plastic film



hydrogen-phosphate peracetic acid and other inorganic salts may be added thereto to provide a proper salt strength and buffering faculty.

The bleach-stabilizing bath contains an oxidizing agent for the developed silver and a complexing agent for the silver ion. Since the former oxidizes the developed silver to silver ion and the latter converts the silver ion into a complex compound or a stable colorless compound, even if such a colorless compound is left in the image in a colorless state, it gives no trouble for practical purposes.

The suitable oxidizing agent is a trivalent iron ethylenediamine tetraacetic acid complex salt, a ferricyanide, or potassium bichromate. As the complexing agent, sodium thiosulfate or sodium thiocyanate is used for the iron ethylenediamine tetraacetic acid complex salt and also sodium thiocyanate is used for other oxidizing agents.

The bleach-stabilizing bath may contain a salt having a buffering action, such as sodium hydrogenphosphate. Furthermore, in the case of using a bleach-stabilizing bath containing the iron ethylenediamine tetraacetic acid complex salt, the fourth step may be omitted.

The processing solution for the final step is an aqueous solution containing sodium sulfite, sodium hydrogenphosphate, borax, and in one case may be sodium thiosulfate, and has the action of improving the quality of the image surface, after processing, and preventing the formation of sticky surface.

By subjecting a color photographic light-sensitive material exposed to the above-mentioned series of processings, the speed for the reversal color photographic developing process is several times faster than that of a conventional rapid reversal color photographic developing process, a desired positive image is obtained in a short period of time, or within 3 minutes, or even within one minute if suitable processing conditions are selected, and, further, the process is very simple.

The merits of this invention, which have never been obtained in conventional techniques, are shown below.

(1) A stabilization process for color photography can be applied to a reversal developing process. A reversal developing process has, hitherto, required final water washing for a long period of time but the inventors have succeeded in applying a stabilization process to the reversal color photographic development as the results of various investigations, whereby the final washing, which takes a long period of time and is required in a conventional reversal developing process, becomes unnecessary. Heretofore, a stabilization process has been applied to only very simple methods of either black-and-white or color photographic processing, but the inventors have succeeded in simplifying the complicated reversal color photographic processing and making the stabilization step effective for reversal color processing.

The reversal color photographic processing can be simplified. A typical process for conventional reversal color photographic processing consists of 10–14 steps, as well as being complicated, and requires a long period of time for finishing all of the steps, whereas the steps can be reduced to 3–6 steps in accordance with the present invention.

The minimum necessary baths in the process of this invention are a black-and-white developing bath, a color developing bath, and a bleach-stabilizing bath, that is to say, by using only the three baths, images fitting practical purposes can be produced by the process of this invention. For stabilizing the process additional steps may be further applied, but even if such addition steps are used, the number of the steps is at most 6, which is far less than the number of steps in a conventional process, and also each step can be finished in a shorter period of time.

(3) The washing step between the black-and-white development and the color development can be omitted. In an ordinary reversal color photographic development, the application of sufficient water washing or stopping after the black-and-white development is necessary. On the other hand, as the results of using the photographic light-sensitive material having a support of low water-absorptive property and finishing the black-and-white developing process in a quite short period of time according to the process of this invention, the reduction in color density and the formation of color stain are not observed as expected even if the color development is conducted directly after the black-and-white development.

(4) The process of this invention has particularly large advantage when it is applied to the light-sensitive materials for drawing, scientific recording, and industrial purposes, and such combinations of the process of this invention and the specific photographic light-sensitive materials are some of the main features of this invention.

(5) Although the process of this invention is not successfully applicable to ordinary color photographic papers, the process can be successfully applied to the thin photographic films and other specific light-sensitive materials having non-water-absorptive supports used for drawings, recording, etc., without forming any color stains.

As the support for the photographic light-sensitive material to be processed by the rapid reversal color photographic process of this invention, films or thin papers having low water-absorptive property are used. As the support for light-sensitive material for drawing, a particularly thin paper or a less water-absorptive water-repellent paper is suitable. Also, as the case may be, a translucent paper, a paper coated with a polymer, such as a polyolefin, for preventing the diffusion of a processing solution, or a resin-impregnated paper is preferably used.

As the photographic emulsion to be applied to the support in this invention, various silver halide emulsion compositions, emulsion layer constructions, and sensitivities can be employed. For instance, as the silver halide composition, there are employed silver chloride, silver chlorobromide, silver iodobromide, and silver chloro-iodo bromide. Ordinarily, a photographic emulsion having a high specific sensitivity is used for a blue-sensitive emulsion layer and emulsions spectrally sensitized and having low specific sensitivities are employed for a green-sensitive emulsion layer and a red-sensitive emulsion layer, but if a high sensitivity is required for the light-sensitive material, a silver halide emulsion (ordinary silver iodobromide emulsion) having such a high specific sensitivity as is being used for camera photographing, may be used for each emulsion layer of the light-sensitive material and a suitable combination of a spectrol sensitization and the application of a yellow filter layer may be applied.

As mentioned before, in regard to the layer structure, one to three silver halide emulsion layers are usually applied to the support and, as occasion demands, intermediate layers and a protective layer are applied. For instance, a dichromatic color photographic light-sensitive material is prepared by applying to the support a blue-sensitive emulsion containing a yellow coupler, an intermediate layer, a green-sensitive emulsion containing a magenta coupler and a cyan coupler, and a protective layer successively. The order of the layer construction of the light-sensitive material may be changed and also the combination of the couplers may be changed with each other. Of course, a trichromatic color photographic light-sensitive material having three silver halide emulsion layers each containing a different coupler and having different spectrally sensitizing regions may be processed in the process of this invention.

The silver halide emulsions used in this invention may be chemically sensitized by a proper combination of sulfur sensitization, reduction sensitization, and gold sensitization. Also, gelatin is usually used as a binder for the silver halide emulsion, but it may contain polyvinyl alcohol, polyvinyl acetate, albumin, or a cellulose derivative highly hydrolyzed.

A hardening agent, an antifoggant, a stabilizer, a surface active agent for coating, and a developing accelerator

usually employed may be added to the silver halide emulsion.

The invention is explained in detail by the following examples.

EXAMPLE 1

A dichromatic color photographic material prepared by applying to a thin photographic paper having a weight of 55 g./m.^{2} for document reproduction a blue-sensitive silver iodobromide emulsion containing a magenta coupler, an intermediate layer of a dispersion of a hydroquinone derivative in gelatin and a silver chlorobromide emulsion containing a cyan coupler and endowed with a green sensitivity by dye sensitization successively was printed by exposure while contacting a two-color line image to the light-sensitive photographic paper and then subjected to the following processings at 40° C.:

	Seconds
Primary development	5
Color development	15
Stopping	10
Bleach-stabilization	20

The compositions of the processing solutions used above were as follows:

Primary developing solution:

Metol (N-methyl-p-aminophenol sulfate) g.	5
Hydroquinone g.	15
Sodium sulfite g.	80
Sodium carbonate·H_2O g.	41
Potassium bromide g.	4
Sodium hydroxide g.	1
Sodium thiocyanate g.	1.5

Water to make 1 liter.

Color developing solution:

Sodium sulfite g.	5
4 - amino - 3 - methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate g.	10
Sodium tertiaryphosphate·12H_2O g.	100
Tri(hydroxymethyl)nitromethane g.	3
Ethylenediamine (70% aqueous solution) ml.	11
Sodium hydroxide g.	0.1

Water to make 1 liter.

Stopping solution:

Sodium sulfite g.	40
Sodium dihydrogenphosphate·2H_2O g.	15
Sodium sulfate g.	120

Water to make 1 liter.

Bleach-stabilizing solution:

Ferricyanide g.	70
Sodium dihydrogenphosphate·2H_2O g.	25
Disodium hydrogenphosphate g.	50
Sodium thiocyanate g.	100

Water to make 1 liter.

By the processing of only 50 seconds, the reproduction of the two-color line image was obtained.

EXAMPLE 2

In the process illustrated in Example 1, the time for the bleach-stabilization was elongated to 40 seconds and as the solution for the bleach-stabilization, the following composition was used.

Bleach-stabilizing solution:	G.
1:1 complex salt of trivalent iron and EDTA	36
Ammonium thiosulfate	100
Sodium sulfite	7
Potassium pyrosulfite	15
Sodium primary phosphate	20
Sodium carbonate·H_2O	6

Water to make 1 liter.

As the result, a good image could be obtained by processing for 80 seconds.

EXAMPLE 3

When the stopping processing in the process of Example 2 was omitted and the following process of 60 seconds was conducted at 40° C., a good line image was obtained.

	Seconds
Primary development	5
Color development	15
Bleach-stabilization	40

EXAMPLE 4

In the process as shown in Example 2, the following step was added to the bleach-stabilizing bath processing:

Stabilization (40° C.) seconds	10
Composition for the stabilization:	
Sodium dihydrogenphosphate·2H_2O g.	50
Sodium sulfite g.	20

Water to make 1 liter.

By the addition of the stabilization step, the stability of the colored image of the reproduced drawing and the physical properties thereof were improved.

EXAMPLE 5

A single layer color photographic light-sensitive material for line image prepared by applying a fine-grain silver chlorobromide positive emulsion containing a cyan coupler to a cellulose triacetate film was exposed and subjected to the following processings to provide a cyan colored reproduction by a process of 33 seconds, in which all processings were conducted at 40° C.

	Seconds
Primary development	3
Color development	10
Bleach-stabilization	20

The compositions of the procesing solutions used in the above process were as follows:

Primary developing solution:

1-phenyl-3-pyrazolidone g.	1
Hydroquinone g.	15
Sodium sulfite g.	30
Sodium carbonate·H_2O g.	30
Potassium bromide g.	2
Sodium hydroxide g.	2
Potassium thiocyanate g.	1

Water to make 1 liter.

Color developing solution:

Sodium sulfite g.	5
4 - amino - 3 - methyl-N-ethyl-N-methanesulfoaminoethylaniline sesquisulfate g.	8
Sodium sulfite g.	55
Sodium tertiaryphosphate·12H_2O g.	30
Ethylenediamine (70% aqueous solution ml.	5
Sodium borohydride g.	0.07

Water to make 1 liter.

Bleach-stabilizing bath:

Same as in Example 2.

EXAMPLE 6

As another embodiment of the example shown in Example 5, the following five steps were applied and a sharp image was obtained. All of the steps were conducted at 40° C.

	Seconds
Primary development	3
Color development	12
Stopping	5
Bleach-stabilization	15
Stabilization	10

The compositions for the above processings were as follows. In addition, the compositions of the primary de-

veloping solution and the color developing solution were the same as those in Example 5.

Stopping solution:	G.
Sodium bisulfite	15
Sodium sulfite	40
Sodium dihydrogenphosphate·$2H_2O$	25
Sodium acetate	30
Water to make 1 liter.	

Bleach-stabilizing solution:

Same as that in Example 1.

Stabilizing solution:	G.
Sodium dihydrogenphosphate·$2H_2O$	30
Sodium thiosulfate	35
Sodium sulfite	30
Water to make 1 liter.	

EXAMPLE 7

In Example 6, the bleach-stabilizing step was conducted for 20 seconds and the final processing was conducted for 10 seconds in the stabilization bath as in Example 4.

What is claimed is:

1. A process for rapidly developing an exposed color reversal photographic material which consists essentially of

(a) black-and-white developing the color reversal photographic material for shorter than 30 seconds, said material comprising a support having coated thereon at least one silver halide emulsion layer containing a color coupler, said support being (1) a paper having a weight of less than 100 g./m.^{2}, (2) a hydrophobic synthetic resin-coated paper, (3) a hydrophobic resin-impregnated paper having a low water-absorbing property or (4) a hydrophobic resin film,

(b) color-developing it for shorter than 60 seconds, and

(c) bleach-stabilizing it for shorter than 60 seconds, said processing steps containing no water-washing step.

2. The process as claimed in claim **1** wherein a stop treatment is carried out between the black-and-white development and the color development.

3. The process as claimed in claim **1** wherein a stabilization step is carried out after the bleach-stabilization.

4. The process as claimed in claim **1** wherein said black-and-white development is carried out for 3–12 seconds.

5. The process as claimed in claim **1** wherein the processing time is approximately 3 minutes.

6. The process as claimed in claim **1** wherein the processing steps are carried out at temperatures higher than 30° C.

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