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PROCESS FOR PRODUCING MULTILAYER COLOR NEGATIVES CONTAINING MASKING IMAGES FOR COLOR CORRECTION PURPOSES

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This invention relates to color photography, and more particularly to a process of producing multi-layer color negatives containing masking images in the cyan and magenta layers for color correction purposes.

In the production of color prints from multilayer color negatives, the color negative consists of yellow, magenta, and cyan images in the different layers. The cyan image represents the red, the magenta image the green, and the yellow image the blue record of the original subject. Color positive prints or transparencies may be obtained from such color negatives by direct printing onto a multi-layer color positive film or paper, or by making color separation negatives which are used for making the color positive prints. These color negatives do not, as a rule, completely satisfy the spectral requirements for trichromatic color reproduction. For instance, the magenta colored image, formed by the imposition of green light upon the green sensitive layer, records the green densities. This image should transmit the blue and the red primaries completely. To the extent to which it absorbs blue light, it superimposes a pattern of the green densities upon the blue, with consequent color falsification. This color falsification makes itself manifest when the color negative is to be printed. That part of the exposure which is due to blue light, and which should form a record only of the image in the yellow layer of the negative, forms a record of the yellow image admixed with the record of the magenta. The image in the blue sensitive part of the copy material, is, therefore, very impure, and serious color degradation results.

It is possible to overcome this defect if procedures are devised to register a pattern of the magenta dye image, equal in intensity to the degree to which the magenta dye absorbs blue light, but opposite in character, with the yellow dye images. In a similar manner, the cyan dye image can be corrected for its blue absorption. These masks or modifying images can be yellow in color, as suggested by the prior art, or they can be a neutral gray, composed of dye or silver.

Numerous methods have been proposed for making corrections in these dye images. Generally, these methods are characterized by the fact that the mask is on a separate piece of film, and must be registered with the original by manual or mechanical means. This creates problems of registry arising from the dimensional variations of film as it ages, and problems of definition arising from lack of optical contact between original and mask, Newton rings, etc. It is desirable, therefore, to have the mask integral with the original. To accomplish this, it has been proposed to place an auxiliary emulsion layer within the pack in which the mask could be formed. While this gives a desirable result, it introduces complications into the structure and the preparation of the monopack material. Since the masking image is opposite in character to the one that it is desired to modify, emulsions with special properties have to be used.

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To eliminate this complication, it was proposed, in British Patent 541,266, to utilize the residual silver-halides in the emulsion after the latent image had been processed to a dye image, and to convert the residual halides, after a proper exposure, into a black and white silver mask. The procedure disclosed, to accomplish the formation of a mask, involved the treatment of the film after negative color development in a bleach bath to convert the silver to silver chloride, removal of the silver chloride by treatment with ammonia or ammonium sulfite, exposure of the untouched residual silver bromide to white light, and development in an M. Q. developer that yields a silver image. When processed in this manner, there are formed silver images in each of the layers of the color film. This may be desirable under certain conditions, but for certain purposes the presence of a mask representing an image of the yellow dye pattern is harmful and undesirable. This was recognized by the British patentee and he specifically states in his specifications that the bleach, to be used to effect a conversion of the silver to silver chloride, be of such a mild nature that it does not destroy the color sensitivities of the green and red sensitive layers. After treatment with such a mild bleach solution, it becomes possible to selectively expose the red and/or green sensitive layers, so that masking images are formed only in these parts.

The restriction that a bleach be used that is so mild that it does not destroy the color sensitivity of the green and red layers, severely limits the operator using the material and the manufacturer who makes it. The patentee cites a number of sensitizing agents that could be used, which will not be destroyed by the extremely mild agents he mentions. But, generally, subjecting an optically sensitized film to the action of an oxidizing agent reduces the color sensitivity of that material almost to the vanishing point. To effect a selective exposure in the green and red sensitive layers would require such long durations as a make the procedure impractical unless special sensitizers be used which are not so affected.

Another method, recently proposed, consists of forming masking images in the original green and red sensitive layers by a reversal processing. The procedure proposed, to accomplish the formation of a mask, is to color develop the exposed multi-layer color film and then subject it to the action of a special fixing bath whose penetration into the depth of the emulsion layer can be controlled and the fixing action thereof limited to the upper-most blue sensitive layer. By this procedure, the residual silver-halides in the blue sensitive layer are removed and can no longer be used to form a masking image, whereas the residual silver-halides in the green and red sensitive layers are substantially unaffected and masking images are formed in these layers upon subsequent exposure and development.

The use of a controlled fixing bath, whose action is limited only to a green layer, presents a complex problem. For instance, it is extremely difficult to prepare such a bath which will have no effect whatsoever upon the residual silver-halides in the other two layers, due to the complication of maintaining a sharp line of penetration as the bath solution becomes absorbed or diffuses through the gelatin.

It is, therefore, an object of the present invention to provide a method for obtaining, in subtractively colored multi-layer photographic color negative materials, masking images composed of silver which correct for the color deficiencies of the cyan and magenta dye images thereof.

A further object is to provide a method for obtaining color corrected color negative materials wherein the color correction is integrally bound with the cyan and magenta dye images.

Other objects and advantages of this invention will be apparent by reference to the following specification, in which its preferred details and embodiments are described.

The foregoing objects are accomplished by developing an exposed, color-developed, bleached, and re-exposed color negative film in the usual black and white developer containing a small quantity of a reagent which will govern the depth at which development will start. These reagents, such as 1-mercapto-benzimidazol, 1-mercapto-benzimidazol-4-sulfonic acid, phenyl-mercaptotetrazol and 2-mercapto-benzthiazol, do not function as developers, or fog-inhibiting agents. Their function is to control the extent below the top surface of the emulsion layer at which development is initiated. During this controlled depth development, the reagents desensitize the upper strata of the emulsion grain layers. The developing solution probably diffuses much faster than the control reagent. Hence, in the deeper sections of the emulsion layers, i. e., the magenta and cyan layers, the developing solution acts normally as though the reagent were absent, since by the time the development action starts, said reagent will have not penetrated to the deeper sections of the emulsion layers. In short, all developing action is stopped in the yellow or uppermost layer, but not in the cyan and magenta layers. As a result of such development, silver images will be produced in the latter two layers but not in the uppermost, yellow, layer. By this controlled depth development, there is achieved the formation of color-correcting silver images in the magenta and cyan layers.

In practicing the present invention, the process involved comprises the following steps:

1. Exposure of the color negative film.
2. Development of the latent images with a color developer.
3. Short-stopping with an acid bath and washing in running water.
4. Bleaching, i. e., converting, of all the silver negative images and any other silver, such as the colloidal silver that may be present in the yellow filter and anti-halation layer, into silver bromide by any bleach bath which does not impair the dye images already present.
5. Exposure of the film to a controlled quantity of white light.
6. Development of the masking images by means of a black and white developer, containing from 0.02 to 0.4 gram of the depth controlling reagent per liter of developer for a period of time ranging from 2 to 10 minutes.
7. Fixation of the unused silver bromide.
8. Washing and drying in the usual manner.

It is to be noted that, during the bleaching of the exposed and color-developed film, the bleach bath reconverts the negative silver images to silver bromide, and these newly formed silver bromide grains are light-sensitive, so that upon re-exposure and development with a developing agent containing these depth controlling reagents, the latent images of silver bromide grains form silver images. The sensitivity of the reformed silver bromide grains is very much less than the sensitivity of the residual silver bromide left after color-development. Hence, ample sensitivity differential exists between the silver bromide formed by the rehalogenation of the negative silver image and the residual silver bromide to allow the formation of latent images only in the residual silver bromide.

It should be pointed out that some of the reagents, hereinbefore described, which control the depth at which development begins, have been utilized in the past as anti-fogging agents in developing baths. All of such reagents which have been used for the latter purpose, however, are not operable in the process of the present invention. Although any black and white developer to which such a reagent has been added may be employed, I prefer those developers which contain hydroquinone, or p-aminophenol as the reducing agent, because they have the least effect upon the dye images formed in the three layers.

The foregoing description of my invention will be more apparent from the following examples which are set forth merely to illustrate and should not be construed as a limitation thereof.

Example I

A multi-layer photographic color film, such as prepared according to U. S. Patents 2,179,228; 2,179,239; 2,186,849; 2,220,187 and 2,357,388, was exposed to a colored object and then developed for 15 minutes in a color developer of the following composition:

Diethyl amino aniline	grams	1.5
2-amino-5-diethylaminotoluene mono HCl	grams	1.0
Sodium sulfite	do	0.5
Sodium carbonate	do	67.5
Potassium bromide	do	2.5
Hydroxylamine HCl	do	0.5
Water to make	liter	1

This development resulted in the formation of negative silver and color images at the exposed portions of the multi-layer film. The color-de-

veloped film was then short-stopped in a 1% solution of acetic acid, containing 1% sodium acetate, and washed for 10 minutes in running water.

After washing, all of the metallic silver in all of the layers was converted into silver bromide by bathing in a bleach bath of the following composition:

Disodium monopotassium ferricyanide	grams	100.0
Potassium bromide	do	15.0
Disodium phosphate	do	40.0
Sodium sulfate	do	22.5
Water to make	liter	1

The bleached film was then washed in running water for 5 minutes.

At this point, the film contains a dye image in each of the three emulsion layers, and silver-halides which cannot be developed unless exposed to light prior to masking development.

The washed film was exposed to the light of a 100 watt lamp at a distance of 5 feet, for a period of 15 seconds, and developed for 2 minutes in a depth developer of the following composition:

p-Aminophenol	grams	5.0
Sodium sulfite	do	40.0
Sodium metaborate	do	40.0
Potassium bromide	do	8.0
1-mercapto-benzimidazol-4-sulfonic acid	do	0.4
Water to make	liter	1

The developed film was then washed, fixed, and dried in the usual manner.

During the masking development, the exposed silver-halides present in the cyan and magenta layers were reduced to metallic silver thereby forming in each such layer a masking image composed of metallic silver to provide for color correction in printing. No development took place in the yellow (uppermost) layer.

Example II

Example I was repeated with the exception that after the bleaching treatment and re-exposure, the film was further developed in a depth developer of the following composition:

Hydroquinone	grams	5.0
Sodium sulfite	do	30.0
Sodium carbonate	do	50.0
Potassium bromide	do	5.0
2-mercapto-benzthiazol	do	0.1
Water to make	liter	1

This development was carried out for 3 minutes so that all exposed silver-halide grains were developed to metallic silver so as to provide masking images in the cyan and magenta layers for color correction and printing.

The developed film was washed, fixed and dried in the usual manner.

Example III

Example I was repeated up to and including a bleaching treatment and re-exposure of the bleached film. The re-exposed film was then developed in a depth developer of the following composition:

Hydroquinone	grams	50.0
Sodium sulfite	do	30.0
Sodium carbonate	do	25.0
Potassium bromide	do	2.0
Phenyl-mercaptotetrazol	do	0.2
Water to make	liter	1

The developed film was then washed, fixed and dried in the usual manner.

The procedure of the foregoing examples has the advantage over other masking methods in that it cuts down the number of processing steps and reduces the time of processing.

Obviously, the practice of the present invention is not to be limited to the processing of multi-layer photographic color film of the type set forth in the examples. Multi-layer photographic film such as prepared according to United States Patents 2,269,158; 2,266,443; 2,272,191; 2,284,877; 2,289,803; 2,304,940; 2,311,020; 2,350,380; 2,397,-864-5-6 and 7, and the like can also be processed into color negatives containing masking images in accordance with the present invention. Various other modifications will occur to those skilled in the art which, however, do not depart from the spirit and nature of this invention and I do not intend to be limited in the patent granted except as required in the following claims.

I claim:

1. In the production of subtractively colored negatives with correction printing masks, integrally bound therein, for multi-layer film comprising an impermeable support bearing superimposed silver-halide emulsion layers containing color-formers and being respectively sensitized to the blue, green, and red regions of the spectrum, the blue sensitive layer being outermost, by exposing said multi-layer film to a colored object, color developing whereby yellow, magenta, and cyan images are formed in the respective layers, bleaching, and re-exposing the same, the improvement which comprises developing the re-exposed silver-halide layers to positive silver images only in the magenta and cyan layers in a black and white developer containing from 0.02 to 0.4 gram per liter of developer of a depth controlling reagent selected from the class consisting of 1-mercapto-benzimidazol, 1-mercapto-benzimidazol-4-sulfonic acid, phenyl-mercaptotetrazol and 2-mercapto-benzthiazol.

2. In the production of subtractively colored negatives with correction printing masks, integrally bound therein, for multi-layer film comprising an impermeable support bearing superimposed silver-halide emulsion layers containing color-formers and being respectively sensitized to the blue, green, and red regions of the spectrum, the blue sensitive layer being outermost, by exposing said multi-layer film to a colored object, color developing whereby yellow, magenta, and cyan images are formed in the respective layers, bleaching, and re-exposing the same, the improvement which comprises developing the re-exposed silver-halide layers to positive silver images only in the magenta and cyan layers in a black and white developer containing from 0.02 to 0.4 gram per liter of developer of a depth controlling reagent consisting of 1-mercapto-benzimidazol-4-sulfonic acid.

3. In the production of subtractively colored negatives with correction printing masks, integrally bound therein, for multi-layer film comprising an impermeable support bearing superimposed silver-halide emulsion layers containing color-formers and being respectively sensitized to the blue, green, and red regions of the spectrum, the blue sensitive layer being outermost, by exposing said multi-layer film to a colored object, color developing whereby yellow, magenta, and cyan images are formed in the respective layers, bleaching, and re-exposing the same, the

improvement which comprises developing the re-exposed silver-halide layers to positive silver images only in the magenta and cyan layers in a black and white developer containing from 0.02 to 0.4 gram per liter of developer of a depth controlling reagent consisting of 2-mercapto-benzthiazol.

4. In the production of subtractively colored negatives with correction printing masks, integrally bound therein, for multi-layer film comprising an impermeable support bearing superimposed silver-halide emulsion layers containing color-formers and being respectively sensitized to the blue, green, and red regions of the spectrum, the blue sensitive layer being outermost, by exposing said multi-layer film to a colored object, color developing whereby yellow, magenta, and cyan images are formed in the respective layers, bleaching, and re-exposing the same, the

improvement which comprises developing the re-exposed silver-halide layers to positive silver images only in the magenta and cyan layers in a black and white developer containing from 0.02 to 0.4 gram per liter of developer of a depth controlling reagent consisting of phenyl-mercaptotetrazol.

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