May 31, 1949. W. H. RYAN ET AL 2,471,547

PHOTOGRAPHIC PROCESS FOR PRODUCING MULTICOLOR IMAGES

Filed Feb. 24, 1947 2 Sheets-Sheet 1

FIG. 1

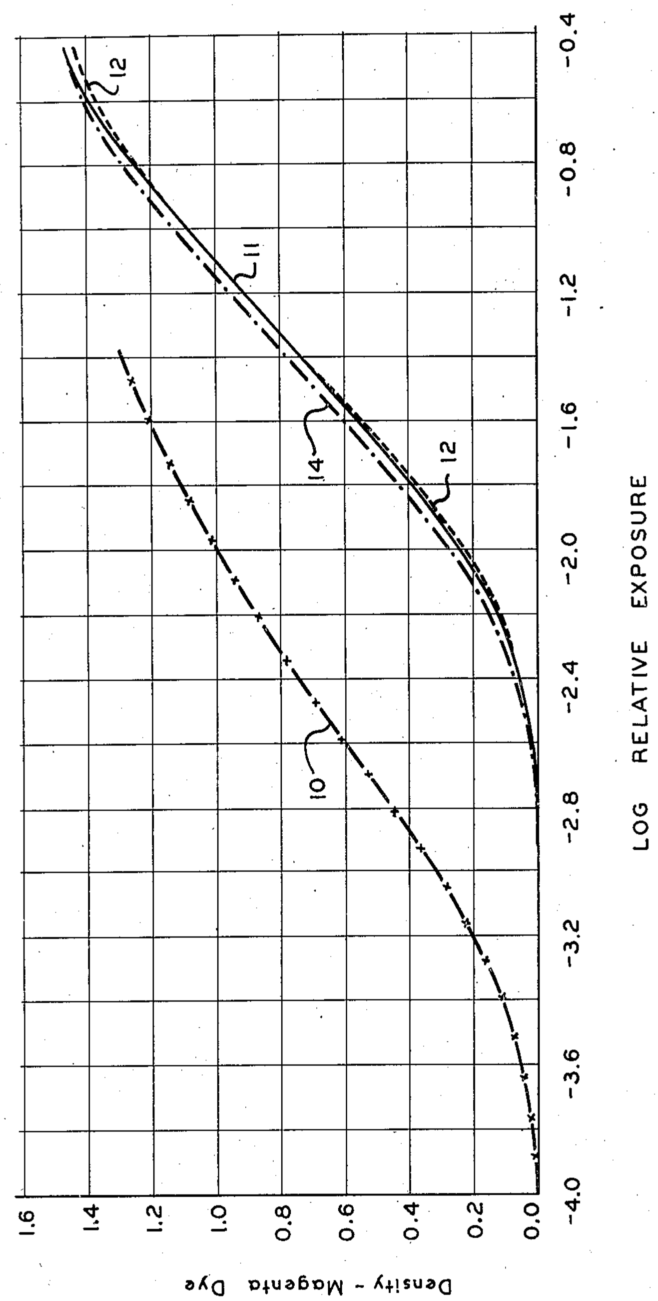

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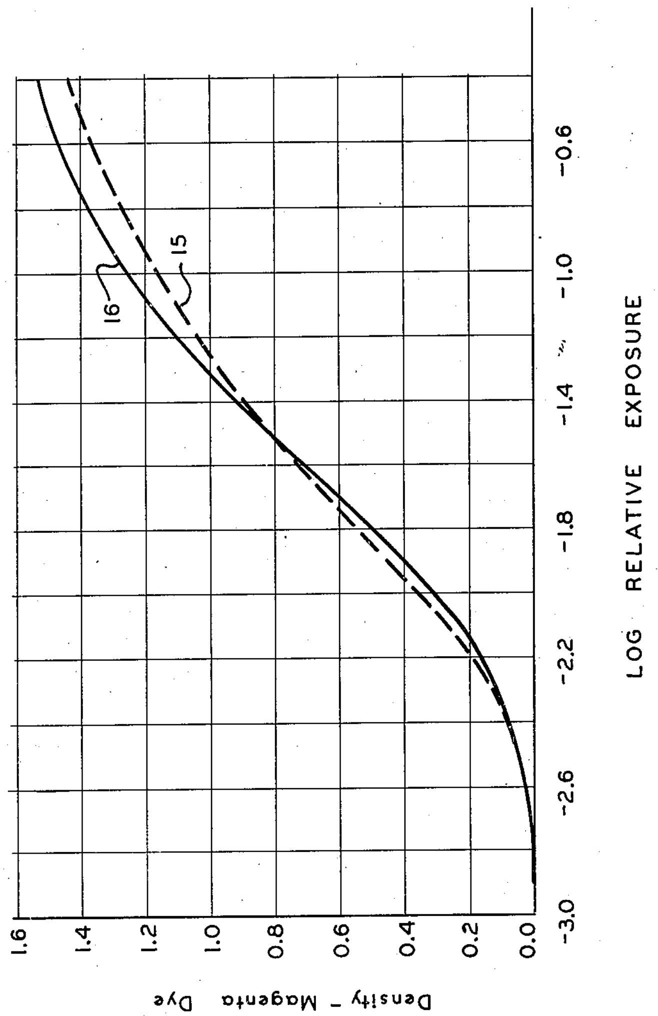
FIG. 2



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PHOTOGRAPHIC PROCESSES FOR PRODUCING MULTICOLOR IMAGES

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Application February 24, 1947, Serial No. 730,274

3 Claims. (Cl. 95—2)

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This invention relates to color photography and more particularly has reference to processes for forming multicolor images, especially processes involving the sequential formation of a multiplicity of dye component images in a single emulsion layer and to improvements in such processes.

Objects of the invention are to provide novel and simplified processes for forming multicolor images as well as processes of this character which are readily controllable and which may be indefinitely repeated with uniform results and also to provide processes designed for multiple copying of multicolor images.

Other objects of the invention reside in the provision of processes involving the sequential formation of dye component images by successive preferential exposures of a single layer emulsion through different color records followed by successive treatments leading to the formation of a multiplicity of dye images in the layer and including practices for equalizing differences in the light-sensitivity characteristics throughout the emulsion during the various stages of processing whereby the emulsion is in a substantially uniform image receptive condition for the sequential formation of each dye component image; and to the provision of processes of this nature wherein developed silver images useful in the formation of dye component images are rehalogenated to light-sensitive silver halide by treatment which will have substantially no effect upon or cause no impairment of dyes used in the processes of the invention.

Still further objects of our invention are the provision of color photographic processes wherein dye component images are formed in sequence in a silver halide emulsion layer from images derived from the sequential exposure of the layer and wherein light-sensitive silver halide is sequentially re-formed in the exposed portions of the layer and the sensitivity of the silver halide in the unexposed portions of the layer is equalized with respect to the sensitivity of the re-formed silver halide; and particularly processes of such character wherein the sensitivity equalization is effected through the controlled uniform exposure of the layer at some stage of processing prior to exposure leading to the formation of a second dye component image in the layer and wherein the layer, without development of latent image formed by such uniform exposure is treated with an oxidizing agent which is capable of destroying latent image without substantially affecting the dye of any component image contained in the

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layer or wherein the layer immediately following the uniform exposure is treated with such oxidizing agent and a halide having the same halogen element as that of the unexposed silver halide and which in combination with the oxidizing agent will react with silver and form silver halide which is developable substantially only upon exposure to light and which is the same halide as the previously unexposed halide while having substantially similar light-sensitivity characteristics therewith.

The invention accordingly comprises the processes involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosures, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Figure 1 shows characteristic density-log relative exposure curves, one of which results from the exposure and development of a photographic emulsion layer with a color-forming developer in the ordinary manner to give magenta dye and the others of which each represents a separate portion of a similar emulsion layer which has been subjected to the special processing and treatment of the present invention, including a controlled uniform exposure, whereby to form magenta dye in these portions of the emulsion layer; and

Fig. 2 shows density-log relative exposure curves for magenta dye formed in separate portions of an emulsion layer like that of Fig. 1 by practices of the present invention but with the omission of a controlled uniform exposure.

In processes of color photography in which silver images, useful in the formation of dye images, are formed in sequence in a single emulsion layer of silver halide, it becomes necessary to restore the silver which comprises the silver images to silver halide which is not spontaneously delevopable. Silver halide which is re-formed from silver in general possesses a lower sensitivity to light than does the original unexposed silver halide in such a layer. To obtain good color rendition it is necessary in such processes to adjust the sensitivity differences or to equalize the sensitivity of the re-formed halide and the portions of the silver halide emulsion which are not previously developed in order to render the emulsion suitably receptive to color component images formed after any exposure and development step in such processes.

Several methods have been provided for accomplishing these effects, the principal one of the prior art involving an exposure sufficient to expose substantially all of the silver halide in the layer to light, developing the halide to silver and re-forming in both the image and nonimage portions light-sensitive silver halide which has essentially uniform light-sensitivity characteristics. The technique of the just-described character, while giving acceptable results, requires additional chemical solutions and washes, thereby adding to the time, expense and intricacy of the color process.

An important feature of this invention resides in the fact that no additional solutions, washes or time-consuming operations, for example, special silver development treatment, are required to effect the adjustment of sensitivity differences in the image and nonimage portions of the emulsion layer and that the techniques herein employed may be conveniently fitted into substantially any multicolor process involving rehalogenation of developed silver.

In a copending application of William H. Ryan for Color photographic processes, Serial No. 721,546, filed January 11, 1947, there has been set forth a color process which involves the successive formation of color component images in a single emulsion layer by color-forming development and through practices which rehalogenate or restore the developed silver image to silver halide in a proper condition for the reception of sequentially formed images. In the process of the just-mentioned application Serial No. 721,546, the reformation of the silver halide from developed silver is effected through action of a rehalogenating composition or compositions which, in addition to converting silver to silver halide, effect the adjustment of inertial difference between the image and nonimage portions of the emulsion and also substantially destroy latent image. By "nonimage portion," we mean that portion of an emulsion which, in the sequential formation of a set of color or dye component images adapted to form a multicolor image, has not been exposed to a color record previous to its exposure for the printing of the second-formed color component image in the series and by "image portion" we mean any portion of the emulsion containing a dye image or a dye image and a silver image or a dye image and silver halide re-formed from silver.

The practice of this invention presents an improvement in the practices set forth in the aforementioned application Serial No. 721,546 in that it renders the image and nonimage portions of the emulsion substantially similar not only in inertia but also in gamma. This improvement is conveniently brought about through the employment of controlled flashing technique used in conjunction with the special rehalogenating treatment set forth in application Serial No. 721,546. Furthermore, the controlled flashing practice permits special adjustment in the characteristics of the nonimage portion of an emulsion by variation in the duration and intensity of the flash whereby a range of development gammas may be obtained.

To this end the present invention preferably renders an emulsion layer substantially uniformly light-sensitive while re-forming substantially nonspontaneously developable silver halide in an exposed and developed silver or image portion thereof by subjecting the emulsion to controlled flashing followed by subjecting the flashed emulsion without development to the action of a rehalogenating composition or compositions which contain an oxidizing agent capable of oxidizing metallic silver to silver ion, substantially destroying latent image and depressing the sensitivity of unexposed silver halide. In fact, it may be said that an oxidizing agent which will destroy latent image will also depress the sensitivity of unexposed silver halide. Oxidizing agents and other materials used with the present invention also possess the property of being substantially inactive with respect to dyes used in forming dye images and especially with respect to photographically useful dyes resulting from color-forming development of latent silver halide, whereby the dyes are substantially unharmed or unimpaired.

It is also important to note that a further feature of our process resides in the fact that the treatment time in the rehalogenating composition necessary to effect the desired adjustment of inertia becomes relatively shorter and less critical than when the heretofore-mentioned controlled uniform exposure is not employed.

As indicated, the practices set forth herein are concerned with the formation, in a single emulsion layer, of one or more multicolor images, through the formation of a set of suitably registered or overlapping dye or color images for each multicolor image in the layer. The invention is useful for multiple copying of multicolor positives, originals, prints and reproductions, especially through the use of suitably prepared color records as, for example, color separation negatives, and is particularly adapted for the copying of motion picture film. At the same time, the processes are suited for use with cut film or with roll film and may be employed in the formation of either positive or negative images.

Conventional photographic films and papers comprising a single emulsion on an opaque or transparent support are suitable for use with the invention to form transparencies or reflection prints. A commercially available film well adapted in the practices of the invention for use as raw stock is ordinary release positive film such as is used for ordinary black and white motion pictures, this being one of the cheapest motion picture films now produced. Films having an emulsion layer on each side of a support, i. e., duplitized film may also be employed. When duplitized film is used, one or more color image components are formed in each emulsion layer of the film. A silver bromide or silver chloride emulsion is employed with film of the character just described and the terms "silver halide" and "silver halides" are used generically herein to refer to both of these light-sensitive substances. Primarily for the sake of convenience and simplicity of processing, the emulsion employed preferably contains only one silver halide and not a mixture thereof.

The rehalogenating practice whereby silver halide is re-formed from silver is carried out by treating an emulsion layer with an aqueous solution of an oxidizing agent and with the appropriate halide ion, the oxidizing agent being capable of oxidizing the metallic silver to silver ion substantially without affecting dyes formed by color-forming development and the halide ion reacting with silver ion to form the desired silver halide. Alternatively, this practice may comprise oxidizing metallic silver to silver ion with an oxidizing agent of the character described, and converting silver ion to an insoluble silver salt which is transformable to the desired silver halide by reaction with the appropriate halide ion.

Preferred oxidizing agents are cupric ion, ferric ion and ferricyanide ion, and compounds providing the same may be found among inorganic and organic compounds comprising cupric chloride, cupric bromide, cupric sulfate, cupric nitrate, ferric chloride, ferric bromide, ferric ammonium citrate, ferric oxalate, sodium ferricyanide, potassium ferricyanide, ammonium ferricyanide and mixtures thereof.

The halide ion which provides the desired silver halide is furnished by a water soluble halide which may be included in the composition containing the oxidizing agent or a developed emulsion may be first treated only with an oxidizer and after formation of the insoluble silver salt may then be treated with the desired halide as, for example, a solution of potassium bromide or potassium chloride.

One example of a suitable rehalogenating composition comprises

Potassium bromide	g	200
Cupric chloride	g	35
Water to make	l	1

Immersion of a developed emulsion in the above composition for about three minutes at about 68° F. will usually be satisfactory for rehalogenating purposes. In the composition just given potassium bromide which furnishes the desired halide ion is included with the oxidizing agent. If desired, treatment of the emulsion may be carried out with separate solutions of oxidizing agent and halide.

In the alternative practice, previously mentioned, an anion other than the desired halide is employed to the end of converting silver ion to an insoluble silver salt which, through an ion exchange reaction with an appropriate halide in aqueous solution is transformed to the desired silver halide. An example of this rehalogenating treatment, which may be carried out in two steps, comprises first immersing a developed emulsion containing a silver image and a dye image in

Solution I

Potassium ferricyanide	g	10
Sodium hydroxide	g	1
Water to make	cc	100

followed by immersion in

Solution II

Potassium bromide	g	10
Water to make	cc	100

Treatments in both Solutions I and II are carried out for about five minutes at about 68° F. The sodium hydroxide in Solution I speeds up the reaction resulting in the formation of insoluble silver ferrocyanide which reacts with potassium bromide to give silver bromide. If desired, the potassium bromide may be added to Solution I and rehalogenation effected in a single step.

As another example of the formation of an insoluble silver salt, a developed silver image may be oxidized with cupric nitrate and treated with sodium sulfate to form insoluble silver sulfate which upon reaction with an appropriate halide will give the desired silver halide.

It is important to note that in all rehalogenating treatments of the invention, the reaction products other than silver halide which result upon the formation of that substance are of a soluble character whereby their removal is readily facilitated.

When rehalogenating silver to silver chloride, equivalent amounts of potassium chloride may be substituted for the potassium bromide in either of the compositions specifically given by way of illustration.

Halides besides potassium bromide and potassium chloride which are useful with the processes of the invention comprise ammonium chloride, ammonium bromide, sodium chloride, sodium bromide and other soluble metal halides.

Commercially available photographic films vary tremendously in their initial light sensitivity. Some are highly sensitized with dyes, for example, while others rely solely on the light sensitivity of the halides themselves. Many films contain mixtures of chloride and bromide or bromide and iodide which enhance the light sensitivity of the emulsion. Commercial films are also normally subjected to ripening and washing operations in the course of their manufacture which increase the sensitivity of the halide. Variations of the character just described will therefore tend to make silver halide re-formed from silver not only differently sensitive from the original halide of the emulsion but, generally speaking, less sensitive. For example, the previously mentioned release positive film is about ten times more sensitive than silver halide re-formed in accordance with the practices of ths invention.

Due to the just-noted fact that most commercial films have a higher sensitivity than re-formed silver halide, the depressant effect on unexposed silver halide by the rehalogenating compositions used by the invention becomes important. As an illustration of this depressant effect, when release positive emulsion is treated with one of the rehalogenating compositions, hereinafter set forth, the inertia of the emulsion may be increased approximately 1 log E unit, and if desired under special conditions may be increased further. With faster emulsions, the effect of the compositions of this invention will also be to reduce sensitivity.

Specifically, with commercially available positive films, the desensitizing action of these rehalogenating compositions is sufficient to bring the sensitivity of the unprinted portions of the emulsion layer within the same range of sensitivity as that of re-formed silver halide, so that multicolor reproductions which are within accepted commercial tolerances of color rendition are obtained. In general, it is considered that an error of approximately ten per cent or less in the density of any color component is acceptable. As a specific example, color tolerances within this limit have been consistently obtained with the use of the heretofore-mentioned release positive film.

The present invention is concerned with a more perfect color rendition than that just mentioned and with one whereby the error in the density of any color component is of a relatively small order. As indicated, this is accomplished by procedure which not only permits an adjustment of inertial difference between the image and nonimage portions of the emulsion but also permits an adjustment of gamma in these portions. When such practice is employed, a color balance is obtained whereby multicolor images are formed which closely reproduce the original colors they are intended to represent.

It has been brought out that the invention is intended for use with any color-forming process wherein a multiplicity of dye component images are formed in a single emulsion layer and in which silver useful in the formation of dye images is restored to silver halide. In this connection, consider an emulsion layer containing light-sensitive silver halide, a color image component comprising a dye and a silver image which is coextensive with the color image component, the only previously exposed portion of the emulsion being that portion in which the silver image and dye image are located. At such a stage, our process proceeds by subjecting the layer to a flash exposure which is controlled as to duration and intensity, following which, and without development, the layer is subjected to the rehalogenating treatment heretofore described. The effect of this procedure is to impart to the layer a sensitivity which closely approaches equality in the various portions thereof.

The exposure to be given by the controlled flash will depend upon a number of factors. For example, exposure will vary in accordance with such factors as the inertia of the initial emulsion, that is to say, the inertia in the nonimage portions thereof, and also with the development gamma desired with reference to subsequent development after the rehalogenating treatment.

For a specific example of controlled flashing, reference is made to the heretofore-mentioned release positive emulsion with which very satisfactory results have been obtained when it is subjected to controlled flashing carried out by moving the film at a rate of thirty feet per minute past a conventional fifteen-watt incandescent bulb located at about two inches from the film or by holding the film stationary and exposing it for one second to a conventional one-hundred-watt incandescent bulb located at about twenty-four inches from the film.

Following the controlled flash exposure and the rehalogenating of silver to silver halide, the layer is in a condition to receive a further dye image component which is formed by suitably exposing the layer, for example through a color separation record, and then treating the layer with one of the rehalogenating compositions to again restore it to a condition receptive for the formation of additional images.

Alternatively, instead of performing the controlled flashing and rehalogenating steps immediately following the formation of the first dye image and when the layer also contains a silver image, if desired, the film may be flashed prior to the formation of any image and subjected to the rehalogenating practices. This latter procedure, as will be apparent, adds additional steps to the photographic processing. It is important to observe, however, that the controlled flash technique need be carried out only once in the practice of this invention for the sequential formation in a single layer of a multiplicity of dye images.

At this point it may be well to repeat that one effect of the controlled flashing and the rehalogenating treatment is to destroy latent image and to restore silver to a light-sensitive nonspontaneously developable condition while lowering or depressing the overall sensitivity of the emulsion or increasing its inertia. A second effect of controlled flashing and rehalogenating

results in a change in the slope of the characteristic curve of the emulsion whereby to equalize sensitivity throughout the emulsion so that the gamma of all parts of a subsequently exposed and developed image will be substantially the same regardless of the portion of the emulsion upon which the image may be printed.

That the two just-mentioned effects take place is evidenced from the characteristic curves shown in the various views of the drawings and which represent characteristic curves of release positive emulsion resulting from various treatments of the same, certain of the curves including treatment by flashing and rehalogenating silver to silver halide.

In Fig. 1, four curves **10**, **11**, **12**, and **14**, are disclosed. Curve **10** represents the characteristics of fresh release positive emulsion which has been exposed to a gray scale, developed in a magenta color-forming developer, subjected to rehalogenating treatment whereby to convert silver associated with magenta dye to silver halide, fixed, washed and dried. The curves **11**, **12** and **14** represent a typical range of conditions which would be expected to occur in the ordinary course of forming a multicolor image in release positive film by the use of controlled flashing in conjunction with the practices set forth in the previously mentioned application Serial No. 721,546 including steps resulting in the formation of the second color image component in such process.

With a multicolor image being formed by successive exposure of a single layer emulsion through color separation negatives, it is preferable to form the successive dye images in the order of the transparency of the dyes to the region of the spectrum in which the emulsion is particularly sensitive. When an essentially ultraviolet- and blue-sensitive emulsion such as silver chloride or silver bromide emulsion is employed, cyan dye will be preferably first formed, followed by formation of magenta dye, which in turn is followed by the formation of yellow dye when three color components are provided.

Curves **11**, **12** and **14** specifically illustrate magenta dye density in three different portions of release positive emulsion. In obtaining data for curves **11**, **12** and **14** one portion of fresh release positive emulsion was given no exposure while two other portions were given graded measured exposures. The portion of the emulsion represented by curve **11** was given no first exposure. The portion represented by curve **12** was first exposed to a gray scale, that is, given a graded exposure varying from no exposure to an exposure equivalent to that required to produce full density in the dye image which is normally first formed in that portion of the emulsion. The portion of the emulsion represented by curve **14** was given a uniform exposure equivalent to that required to produce full density in the dye image which is normally first formed in that portion.

The two portions of the emulsion containing latent image were then developed in a black and white developer approximating the characteristics typical of a cyan color-forming developer in that it provides silver of equivalent density to silver resulting from cyan color-forming development. For example, a color-forming developer could be employed without the use of a coupler. Color-forming development of these two portions of the emulsion was not employed since the presence of a dye image would make it difficult to obtain accurate measurements of the characteristic curves of subsequently formed images. It is to be noted that the two portions subjected to the just-described development may be said to have a first image formed therein.

Following the just-described development, the two portions of the emulsion having silver therein were treated in a stop bath, washed, and subjected to a controlled flash exposure followed by treatment in a rehalogenating composition prior to any further development, after which these portions were washed, treated in a clearing bath, washed and dried. At this stage the two portions of the emulsion subjected to the foregoing treatment contained unexposed silver halide in the nonimage part thereof and silver halide which was re-formed from silver in the image or the previously exposed part thereof.

The third portion of the emulsion, namely that portion which was given no first exposure and development, and which is illustrated with reference to curve 11, was given the controlled flash exposure of this invention and without development subjected to the action of the oxidizing agent of one of the rehalogenating compositions previously disclosed by immersing that portion of the emulsion in such a rehalogenating composition, following which this portion of the emulsion containing no image was treated in a clearing bath, washed and dried.

Magenta dye was then formed in all three portions of the release positive emulsion by exposing each portion to a gray scale and developing in a magenta developer. Silver associated with the magenta dye was removed by rehalogenating treatment to form silver halide and each of the three emulsion portions were fixed, washed and dried.

The dye densities in the three portions of the emulsion which were respectively given no exposure and graded exposures and the combined flashing and rehalogenating treatment were measured by a photoelectric instrument whereby to obtain data for the curves 11, 12 and 14. Similarly, the dye density in the portion of the film which was not subjected to the practices of this invention but was merely exposed and developed with the magenta color-forming developer was measured by a photoelectric instrument for the plotting of the curve 10. It is to be kept in mind that the densities given in curves 10, 11, 12 and 14, and for that matter in all curves shown in the drawings, were measured by a photoelectric instrument and that the measured densities do not correspond with visual densities.

A study of the curves in Fig. 1 clearly shows by the horizontal displacement of curves 11, 12 and 14 from the curve 10 that the inertia of the emulsion is increased following the flashing and rehalogenating practices discolsed herein, it being kept in mind that curve 10 represents the characteristics of fresh emulsion which was exposed to a gray scale and which contained only a magenta image but which was not subjected to the processing of this invention. This increase as disclosed is approximately equal to 1 log E unit.

Furthermore, curves 11, 12 and 14 show the second effect of controlled flashing and rehalogenating practice, namely, the equalization of sensitivity throughout the emulsion whereby the gamma of all parts of any image exposed and developed after the first dye component image will be substantially the same regardless of that portion of the emulsion upon which such subsequent image is printed. In this regard it is to be noted that curves 11, 12 and 14 are of the same relative shape and lie closely parallel to each other, from which fact it becomes evident that density disparities are reduced to negligible differences between portions of the emulsion representing the initial silver halide and portions in which a silver image has been formed and subsequently rehalogenated to silver halide and which coupled with the increase in inertia renders the emulsion substantially uniformly receptive for the formation of subsequent dye images whereby to permit faithful color rendition.

As further evidence of the improvements effected by this invention whereby color balance for multicolor images may be obtained, reference is made to Fig. 2 and to the curves 15 and 16 thereof representative of characteristic curves for release positive emulsion, one portion of which, represented by curve 15, has been subjected to processing such as that resulting in the curve 11 but without the controlled flashing step of the present invention, the portion represented by the curve 15 having no first exposure image formed therein. On the other hand, the curve 16 of Fig. 2 was obtained by the treatment of a portion of the emulsion through processing practices similar to those outlined in connection with curve 14 of Fig. 1 and also without employment of the controlled flash procedure but with the formation of a first image of uniform full density therein.

While curves 15 and 16 indicate that an increase of inertia is obtained through the use of the oxidizing agent of the rehalogenating composition, they show that there is some disparity in the gammas of the unexposed and the exposed portions of the emulsion. This is apparent from the fact that curves 15 and 16 are not closely parallel to each other and that the over-all separation between them is considerably wider than between the curves 11, 12 and 14 of Fig. 1. This separation, while within the previously mentioned commercially accepted standard of a ten per cent difference in density, obviously lacks the close color balance permitted when combining flashing and rehalogenating practices in a process for the sequential formation of color component images whereby to produce a multicolor image.

The practices herein set forth broadly constitute an improvement of color processes which sequentially form dye component images in a single-layered emulsion and which involve reforming silver halide from silver useful in the formation of the dye images. In this regard the controlled flashing and rehalogenating techniques may be fitted into any color process of the character heretofore noted. For example, controlled flash exposure and rehalogenating practices such as we have disclosed may be used in processes wherein a silver image printed from a color record is converted to a dye mordant and after the mordanting of a dye thereto is reacted to form silver or a silver salt from which desired silver halide may be re-formed by treatment in a rehalogenating composition or compositions such as are described herein. Our flashing and rehalogenating practices are especially adapted for use with and are conveniently fitted into the color photographic process of application Serial No. 721,546, which makes use of sequential color-forming development. Accordingly, and by way of completely describing our invention, a specific process involving sequential color-forming development and leading to the formation of three-color or dye component images will be detailed through the use of positive film such as release positive motion picture film. The steps in complete processing are as follows:

1. Expose positive film through cyan printer negative (red separation negative).

2. Develop for four minutes in a cyan color-forming developer of the following formula:

Sodium carbonate, des	g	25
Sodium sulfite	g	1
p-Diethylaminoaniline monohydrochloride	g	0.6
Potassium bromide	g	0.4
2,4-dichloro-1-naphthol	g	1
Acetone	ml	100
Water to make	l	1

The result of this development is to form a silver image and a cyan dye image exposed in the portion of the emulsion layer of the film.

3. Immerse for one minute in stop bath having the following formula:

Sodium carbonate, des	g	2.2
Paraformaldehyde	g	5
Water to make	l	1

Alternatively, other types of stop baths may be employed, such, for example, as bisulfite or buffer solutions with a pH of 4.5 to 6 for limited times of treatment.

4. Wash in running water for three minutes.

5. Give film a controlled flash exposure.

As previously mentioned in the case of release positive motion picture film, exposure may be made by a conventional fifteen-watt incandescent bulb located at about two inches from the film which is moved past the bulb at the rate of thirty feet per minute or, when the film is held stationary, exposure is for one second to a conventional one-hundred-watt incandescent bulb located at twenty-four inches from the film.

6. Treat for three minutes in the following solution:

Potassium bromide	g	200
Cupric chloride	g	35
Water to make	l	1

Step 6 is the rehalogenating treatment previously described and a result of carrying out this operation is to re-form silver halide in any exposed portion of the film and following such treatment the emulsion layer contains silver halide throughout and the component image formed of cyan dye, the silver halide being substantially uniformly sensitive and developable only upon exposure to light.

7. Wash for three minutes.

The purpose of this washing step is to remove any residual traces of rehalogenating composition, including oxidizing agent, and any soluble reaction products of the rehalogenating treatment. If desired, prior to washing, the film may be subjected to a clearing bath, for example a clearing bath comprising bisulfite, the treatment in such a bath being for a limited time whereby to leave any dye component image present in the film substantially unaffected.

8. Dry.

9. Expose film to magenta printer negative (green separation negative) in proper register.

10. Develop for three and a half minutes in magenta color developer having the following formula:

Sodium carbonate, des	g	12.5
Sodium sulfite	g	6
p-Diethylaminoaniline monohydrochloride	g	.4
Potassium bromide	g	.25
p-Nitrophenylacetonitrile	g	.25
Acetone	g	25
Water to make	l	1

Following exposure and development to provide the magenta image, the emulsion layer contains light-sensitive halide, the cyan component image, the magenta component image and also developed silver.

11 through 15. Steps following this development are the same as those following the cyan color development with the omission of the controlled flashing of step 5 but including the practices of steps 3, 4, 6, 7 and 8.

Following reconversion of silver to silver halide by step 13 in the process, the emulsion layer contains light-sensitive silver halide throughout, the cyan component image and the magenta component image, but no silver.

16. Expose film to yellow printer negative (blue separation negative) in suitable register.

17. Develop in yellow color developer having the following formula:

Sodium carbonate, des	g	50
Sodium sulfite	g	5
p-Diethylaminoaniline monohydrochloride	g	3
Potassium bromide	g	2
Ethyl acetoacetate	ml	20
Acetone	ml	80
Water to make	l	1

Following the yellow development, the emulsion layer contains light-sensitive silver halide, the cyan component image, the magenta component image, silver and the yellow component image.

18 through 20. The next three steps are the same as those following the cyan color development with the omission of the controlled flashing of step 5 but including the practices of steps 3, 4 and 6.

The effect of rehalogenating in step 20 is to convert silver to light-sensitive silver halide to the end that the emulsion layer contains light-sensitive silver halide throughout and cyan, magenta and yellow dye components which together form at least one multicolor image.

After step 19, that is, washing after treatment in a stop bath such as that illustrated in step 3, the silver in the film may be removed or destroyed by any practice which does not harm the dye images. A convenient manner of accomplishing this is to rehalogenate the silver to silver halide which leaves the entire emulsion layer in a condition wherein substantially all substances except the dye images may be removed by conventional fixing baths followed by washing and drying. Alternatively, after step 20 a silver sound track or other auxiliary silver image may be formed in the emulsion layer of the film by procedures such as those set forth in the copending application of William H. Ryan for Color photographic processes for producing multicolor images and associated auxiliary images and products thereof, Serial No. 721,548, filed January 11, 1947.

As regards to dyes formed by color-forming development, our invention intends to make use of any photographically useful dye of this character. Typical examples of dyes which may be employed are represented by those used in Kodachrome, Ansco Color, and Kodacolor processes. It is important to observe that dyes resulting from color-forming development are in general more highly subject to attack by oxidizing agents, acids, and other reagents and substances than are mordant dyes useful for photographic purposes.

Nondichroic dyes and dichroic dyes may be formed by color development and both classes are included within the scope of this invention. Dichroic dyes are especially suited for the formation of light-polarizing images and are useful in the practice of vectography. A dichroic dye as distinguished from a nondichroic dye will form a dichroic sorption complex with a molecularly oriented plastic and will differentially absorb incident light when incorporated in the plastic. Suitable plastic materials in the form of linear high polymers are hereinafter named.

As specific examples of nondichroic dyes resulting from the color development of exposed silver halide mention may be made of azomethine, indoaniline, indophenol, indanthrene and indamine dyes. These may be formed by so-called "primary developers" which directly form colored compounds in the development of latent silver halide to silver as well as by so-called "secondary developers" which when oxidized and reacted with a coupler will form colored compounds.

Many dyes which display suitable dichroism and which are of appropriate color may be found among the azo dyes and these may be formed through the use of developers from the class of organic compounds known as hydrazines. The primary aromatic hydrazines provide both primary and secondary developers especially suited for this purpose and as examples thereof mention may be made of phenylhydrazine; bromo and chloronaphthylhydrazines; tolylhydrazines; nitrophenylhydrazines; bromo and chlorophenylhydrazines; α-naphthylhydrazine; p,p'-diphenylhydrazine; methoxyphenylhydrazines; p-carbethoxyphenylhydrazine; and the like. Generally speaking, wherever couplers are employed with hydrazines which form secondary developers, compounds corresponding to the couplers useful in forming nondichroic dyes may be employed.

In the practice of this invention, the carrier in which the emulsion is dispersed may be formed of any suitable hydrophilic material. Materials of this nature comprise gelatin and transparent, hydrophilic, high molecular weight, linear polymers which may have their molecules oriented and which form a dichroic sorption complex with certain organic dyes, as well as other materials suitable as emulsion carriers.

If the molecules of a high linear polymer are oriented and an image is formed therein comprising a dichroic dye, the image will be light-polarizing in character and the invention is intended to include this concept within its scope. As specific examples of suitable long-chain, hydrophilic, transparent plastics which may have their molecules oriented, mention may be made of polyvinyl alcohol, polyhydroxy alkane, partially hydrolyzed polyvinyl acetals and polyvinyl alcoho esters, amylose, regenerated cellulose, and suitably prepared polyamides or nylon-type plastics.

Gelatin and polyvinyl alcohol may be named as preferred carrier materials.

Although the term "halogenating" is customarily used in organic chemistry in a narrower sense than it is employed herein, it is employed to mean the step of forming silver halide from silver and "rehalogenating" is used throughout the specification and claims to define the step of forming silver halide from silver which has at some previous stage been derived from a silver halide.

While having its principal usefulness in the field of three-color photography, our process should not be construed as limited to the formation of three-color images and sound track, as heretofore described. The practices of the invention may be used for the formation of two-color pictures with or without sound track; for the formation of so-called anaglyph pictures for stereoscopic purposes; for the formation of light-polarizing images which may be employed for stereoscopic purposes; or in general for the formation of any plurality of images in a single emulsion layer for any purpose.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process of color photography which comprises exposing an emulsion layer containing light-sensitive material comprising at least one silver halide selected from the class consisting of silver bromide and silver chloride and forming therein a latent image representative of a color component of a multicolor image; developing said latent image with a color-forming developer which forms a dye image and a silver image in said layer; giving the layer a controlled uniform exposure to light; without development of latent image created by said uniform exposure, treating said layer by subjecting the layer to the action of only one soluble halide which is reactable with silver ion to form silver halide and which is selected from the class of halides consisting of soluble bromides and soluble chlorides, and an oxidizing agent which is substantially inactive with respect to image dye and which in the presence of the soluble halide selected from said class of soluble halides, possesses the properties of effecting formation from silver of silver halide having a halogen element which is the same as that of said soluble halide, of destroying latent image, of reducing the sensitivity of unexposed silver halide and of forming reaction products other than said silver halide which are soluble whereby the light-sensitive material of said layer essentially comprises silver halide having the same halogen element as said soluble halide and possesses substantially uniform but lower sensitivity than the light-sensitive material of said layer prior to any exposure thereof; forming in the layer in register with said already-formed dye image at least one other latent image representative of another color component of said multicolor image and developing the last-mentioned latent image with a color-forming developer which forms in said layer a silver image and a dye image having a color different from that of said first-mentioned dye image; and when multicolor image formation is concluded removing substantially all silver and silver salts from said layer.

2. A process of color photography which comprises exposing an emulsion layer containing substantially only silver bromide to a color component image; developing said layer with a color-

forming developer which forms a silver image and a dye image in said layer; exposing the layer substantially uniformly to light; without development of latent image created by said uniform exposure, treating said layer by subjecting the layer to the action of a soluble bromide which is reactable with silver ion to form silver bromide and an oxidizing agent which is substantially inactive with respect to image dye and which in the presence of said soluble bromide possesses the properties of forming silver bromide from silver, of destroying latent image, of reducing the sensitivity of unexposed silver bromide and of forming reaction products other than silver bromide which are soluble, whereby the light-sensitive material of said layer essentially comprises silver bromide and possesses substantially uniform but lower sensitivity than the light-sensitive material of said layer prior to any exposure thereof; exposing said layer to a second color component image in register with the dye image in said layer; developing the layer with a color-forming developer which forms in said layer a silver image and a dye image having a color different from that of said first-mentioned dye image; without any exposure of the layer subjecting said layer, including the last-mentioned silver image, said dye images and residual silver bromide, to the action of said oxidizing agent and said soluble bromide; exposing said layer to a third color component image in register with the dye images in said layer; developing the layer with a color-forming developer which forms a silver image and a dye image having a color different from that of said first- and second-mentioned dye images; and substantially freeing the layer of silver and silver salts remaining therein.

3. A process of color photography which comprises exposing an emulsion layer containing substantially only silver chloride to a color component image; developing said layer with a color-forming developer which forms a silver image and a dye image in said layer; exposing the layer substantially uniformly to light; without development of latent image created by said uniform exposure, treating said layer by subjecting the layer to the action of a soluble chloride which is reactable with silver ion to form silver chloride and an oxidizing agent which is substantially inactive with respect to image dye and which in the presence of said soluble chloride possesses the properties of forming silver chloride from silver, of destroying latent image, of reducing the sensitivity of unexposed silver chloride and of forming reaction products other than silver chloride which are soluble, whereby the light-sensitive material of said layer essentially comprises silver chloride and possesses substantially uniform but lower sensitivity than the light-sensitive material of said layer prior to any exposure thereof; exposing said layer to a second color component image in register with the dye image in said layer; developing the layer with a color-forming developer which forms in said layer a silver image and a dye image having a color different from that of said first-mentioned dye image; without any exposure of the layer subjecting said layer, including the last-mentioned silver image, said dye images and residual silver chloride, to the action of said oxidizing agent and said soluble chloride; exposing said layer to a third color component image in register with the dye images in said layer; developing the layer with a color-forming developer which forms a silver image and a dye image having a color different from that of said first- and second-mentioned dye images; and substantially freeing the layer of silver and silver salts remaining therein.

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