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CONTROLLING GRAIN AND CONTRAST IN COLOR PHOTOGRAPHY

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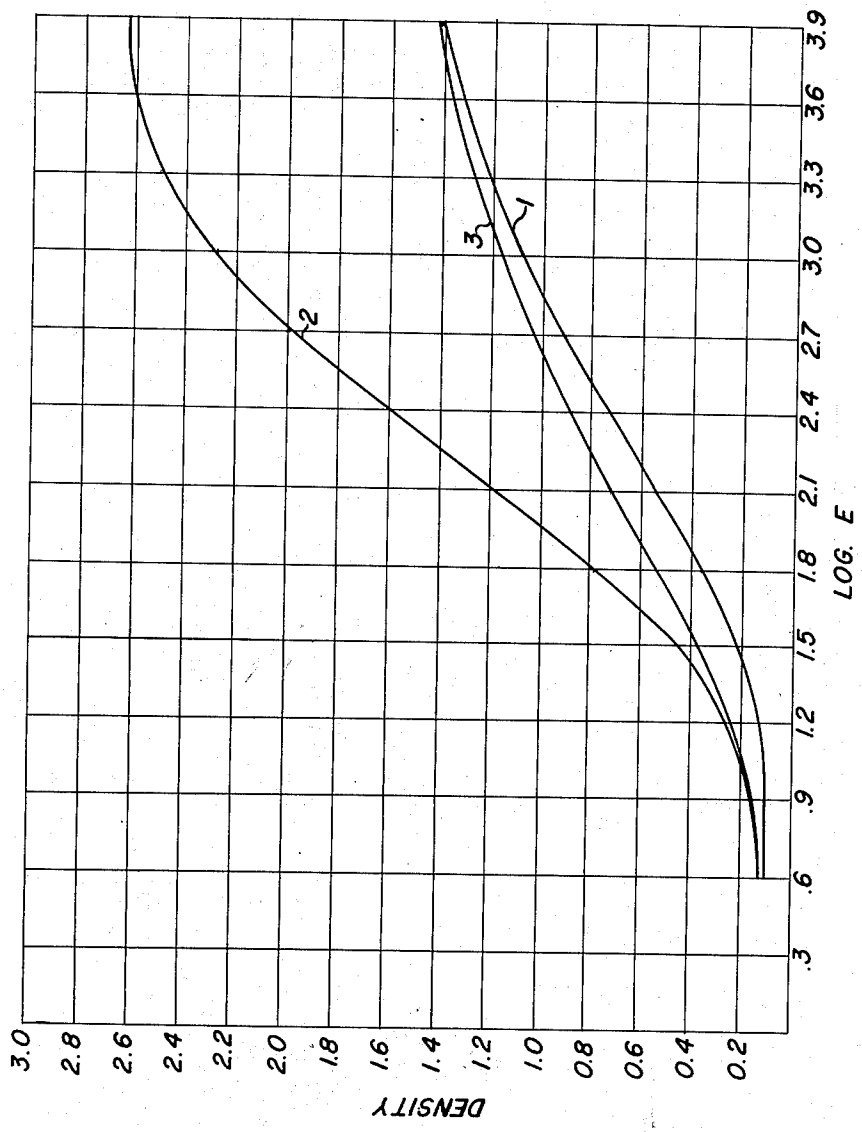

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CONTROLLING GRAIN AND CONTRAST IN COLOR PHOTOGRAPHY

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This invention relates to a process for controlling the graininess, sharpness and contrast characteristics of dye images in color photography.

In well-known processes of color photography the dye images are produced in silver halide emulsion layers by exposing to colored subjects and developing the resulting latent images with a primary aromatic amino silver halide developing agent in the presence of coupler compounds which react with the oxidized developing agent to form dyes. In such a process of dye image formation, commonly called color development, the dyes which are formed generally have relatively very high covering power. Thus for a given number of moles per unit area of the image, a dye image prepared by color development exhibits a much higher density to light in the wavelength region corresponding to its absorption band than does a silver image. For this reason a conventional emulsion layer, which on normal black-and-white processing yields a normal contrast silver image, produces a dye image on color development which has such excessive contrast that it is not usable in a color photographic process.

In order to overcome this intensification effect of color development, it is usually necessary to reduce the amount of silver halide in the emulsion layers to such a point that the dye images formed on color development have the required normal contrast values. In practice it has been found that this leads to the use of very low amounts of silver halide in the emulsion layers relative to the amounts normally used in conventional black-and-white sensitive materials. Serious and undesirable consequences of such a reduction in silver halide content of the emulsion layers are that the color-developed dye images have a very coarse-grained structure and a loss in image sharpness and definition occurs.

It would appear that this difficulty might be circumvented by using silver halide emulsions which are inherently finer grained so that the emulsion layers would have the same total silver halide content distributed among a larger number of grains. Unfortunately, this simple solution cannot be realized in those cases where emulsion speed is of importance, because the speed of a silver halide emulsion is, in general, directly related to the grain size. Accordingly, for those color photographic materials where high emulsion speed is a necessary property, the relatively coarser-grained silver halide emulsions must be employed and alternative solutions to the problems of graininess, and sharpness and definition of the dye images must be sought.

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We have now discovered that a solution to this problem is attained when the silver halide emulsion layers containing relatively large amounts of silver halide are color developed in the presence of an agent which is capable of reacting with the oxidized developing agent, with the result that a portion of the total oxidized developer formed during development is rendered unavailable for dye image formation. In effect, the added agent competes with the coupler for the oxidized developer and thereby permits the formation during color development of an amount of oxidized developer in excess of that required to produce dye images of normal contrast. This, in turn, permits the use of larger amounts of silver halide in the emulsion layers, and as the end result one obtains dye images of the desired normal contrast which do not have the exaggerated graininess and low sharpness and definition which characterize the images produced by conventional color development procedures.

One object of our invention, therefore, is to provide a process for obtaining dye images with improved graininess and sharpness characteristics. A further object is to provide a method for obtaining dye images of normal contrast by color development of silver halide emulsion layers which contain amounts of silver halide in excess of that required for the production of dye images by conventional color development procedures. Other objects will become apparent from the following more detailed description of our invention.

The objects of our invention are preferably accomplished by using, for the formation of colored photographic images, silver halide emulsion layers containing amounts of silver halide in excess of those required to produce images of normal contrast when conventional color development is carried out, and conducting the color development of such emulsion layers in the presence of a compound, referred to hereinafter as a competing coupler, which competes with another coupler present for the oxidized developer. The competing couplers appear to react with the oxidized developing agent to produce a dye which is soluble and removable from the emulsion layer by washing.

Color development processes utilizing color development as the means of dye image formation are conveniently divided into two classifications, which differ in the method of introducing the

couplers into the system. The first type of such processes makes use of couplers which are soluble in the color developer solution and which are diffusible into the silver halide emulsion layers. Here the dye-forming reactions occur between two components of the color developer solution to produce a dye which is insoluble and/or nondiffusible. In the second type of color processes, nondiffusing couplers are incorporated in the silver halide emulsion layers and the coupling reactions occur between these incorporated couplers and the primary aromatic amino developing agent supplied from the color developer solution as shown in Mannes et al. U. S. Patent 2,304,940 and Jelley and Vittum U. S. Patent 2,322,027. Our invention is applicable to both types of color processes. In the first type of process which employs soluble diffusible couplers, the color developer solution contains the color developing agent, the dye-image-forming coupler, and the competing coupler. With the color process employing incorporated nondiffusing couplers, the developer solution contains the color developing agent and the competing coupler, or alternatively, the competing coupler can also be incorporated in the silver halide emulsion layers.

As used herein, by "diffusible coupler" is meant one which can be incorporated in the developer and which forms a soluble dye which quickly diffuses out of the emulsion layer, and by "soluble but non-diffusing coupler," is meant one which can be incorporated in the developer, but forms a comparatively permanent, nondiffusing dye.

The accompanying drawings show, by means of graphical representation, the effect upon contrast of utilizing the diffusible competing coupler in the development of a high concentration coarse-grained emulsion containing a nondiffusing coupler compound.

Color development has previously been carried out in the presence of a mixture of couplers in emulsion layers as disclosed in U. S. Patent 2,186,736, granted January 9, 1940, to obtain a colored image and in U. S. Patent 2,428,054, September 30, 1947, and South African Patent 1,240 of 1946. However, these patents contemplate the use only of couplers which are non-diffusible in emulsion layers and do not contemplate the use of non-diffusing couplers in emulsions developed by color developer compositions containing diffusible couplers as in the present invention. Similarly, our invention is separate and distinct from any known use of a mixture of soluble and diffusible couplers in color developing solutions that form images of nondiffusing dyes.

Our invention will now be described in more detail in the following example with particular reference to the accompanying drawings:

A fast coarse-grained red light-sensitive emulsion is prepared and a non-diffusing coupler compound 2-(diamylphenoxyacetamido)-4,6-dichloro-5-methyl phenol is dispersed therein by the methods of the above Jelley and Vittum invention. The concentration of silver halide and coupler compound in the emulsion are so adjusted that when the emulsion is coated on to a suitable film base, 60 milligrams of coupler and 30 milligrams of silver halide (calculated as silver) are obtained per square foot of coating. This represents a quantity of silver halide which will yield, upon color development, a cyan dye image of useful contrast although having more grain than desired. The emulsion layer is then exposed to the red aspect of a colored subject and developed for 9 minutes in an ordinary color-forming developer solution such as that shown in the mentioned patent but devoid of coupler compounds. Development is then followed by removal of the silver image obtained during development to yield a cyan dye image, the contrast of which is illustrated by the density-log E curve 1 of the drawings. The contrast of this image is comparable to contrasts of dye images obtained in widely used color processes; however, the graininess of the cyan dye image is more than desired.

A similar emulsion is prepared in the manner of the mentioned patent having a considerably higher silver halide concentration per unit area such that when it is coated on to a film base the silver concentration is 400 milligrams per square foot and the coupler concentration 60 milligrams per square foot of coating (the same coupler concentration as that of the first emulsion prepared above). After exposure as above, development is carried out in the same color developing composition for 6 minutes and the silver image is removed. Curve 2 shows the high contrast of the cyan dye image obtained by increasing the silver concentration of the emulsion from 30 to 400 milligrams per square foot.

According to our invention, when there is now added to the color developing solution, 2.5 grams of the diffusible coupler compound 1-amino-8-naphthal-3,6-disulfonic acid (H-acid) and the second emulsion is developed in this composition for 11 minutes followed by the usual silver removal steps involving use of an oxidizing bleach bath, followed by treatment with hypo and washing, curve 3 shows that the contrast of the cyan dye image obtained is substantially that of the color process represented by curve 1. In addition, a comparison of the grain characteristics shows that the grain has been materially reduced by the use of the diffusible coupler compound in the developer composition. Presumably grain has been improved because more development centers are made available by using the higher silver halide concentration and because the dye does not appear to wander from these development centers as in the case of emulsions containing relatively little silver halide.

Comparable results are obtained when the process is carried out by reversal in which the emulsion is first developed in a black and white developer followed by reversal exposure and development with the color developing solution containing the diffusible coupler compound. For example, two differentially sensitized multilayer color elements each containing in the respective emulsion layers, substantially nondiffusing coupler compounds were prepared by the methods of the above U. S. Patents 2,304,940 and 2,322,027. The two elements were similar in all respects except that each emulsion layer of the first element contained from two to four times as much silver halide as the corresponding emulsion layer of the second element. The two elements were then exposed to a colored subject and developed in a black-and-white developer. Following reversal exposure each element was then developed under the same conditions in a color developer of the same composition except that the color developer for the first element was modified solely by adding .075 g. per liter of 1-naphtol-3,6,8-trisulfonic acid. The elements were then both subjected to the usual silver bleach and fixing steps. Under these processing

conditions the two coatings gave dye images having very nearly the same contrast and color balance; however, the first element which had higher silver content and which was developed in the color developer containing the diffusible coupler compound, showed about .4 log E higher speed, much higher sharpness and definition, and less graininess than the second element.

Our process is primarily designed for, although not limited to use in systems of color photography employing superposed emulsion layers sensitized to the primary regions of the visible spectrum and containing in the respective emulsion layers non-diffusing coupler compounds yielding differently colored dye images. When our invention is employed as described with these superimposed emulsion layers and development is carried out in a color-forming developer composition containing a soluble competing coupler yielding a diffusible dye, the contrast and grain characteristics of the dye images in all emulsion layers are improved substantially as illustrated in the drawings. Such films may be utilized in the well-known negative-positive and reversal color development processes in the manner described in the above examples.

The silver halide concentration per unit area of the emulsion layers employed in our invention is that necessary to reduce the contrast and grain to the desired value and can be varied within rather wide limits depending upon the result desired and the particular process which is under consideration. Substantial improvement in grain characteristics is obtained by using at least about 50 milligrams per square foot of emulsion and preferably about 2 to 25 times the usual silver halide concentration of incorporated coupler processes, or from about 50 to 750 milligrams of silver halide (calculated as silver) per square foot of emulsion. As is apparent, if the emulsions contain substantially more than about 50 milligrams silver per square foot, normal color development in absence of diffusible coupler compounds yields greater contrast than usually desired in color processes.

The quantity of competing diffusible coupler which is used in the color developing compositions is dependent upon a number of factors. One of these is the relative coupling activity of the non diffusible couplers compared to that of the diffusible competing couplers. In a given color system a suitable type and quantity of competing coupler can be readily ascertained. Another factor is the contrast desired in the particular color process under consideration. That is, in a color printing process a contrast of 2.5 may be desired, whereas in a negative color process such as illustrated in the above example, a contrast of only about 0.7 may be desired. More competing diffusible coupler can be employed in conjunction with the latter process to effect a greater reduction in contrast. We naturally use sufficient diffusible competing coupler in the developer composition that after color development of the emulsion layers containing coupler compound followed by washing out the diffusible dye image, there are obtained non-diffusible dye images having the contrast of the process under consideration, such as contrasts of the order of about 0.5 to 2.5.

In connection with multilayer color films for which our process is particularly adapted, these color films may contain in the respective emulsion layers non-diffusible couplers of different coupler activity. Therefore, the relative increase in the silver halide concentration required in the emulsion layers may differ depending upon the coupling characteristics of the couplers in each emulsion layer.

The diffusible coupler compound, H-acid, employed in the above example is especially efficacious for use in the process of our invention. Other suitable diffusible coupler compounds are the following:

1-amino-8-naphthol-3,6-disulfonic acid — "H-acid"
2-amino-5-naphthol-7-sulfonic acid—"J-acid"
1,8-dihydroxynaphthalene disulfonic acid—chromotropic acid
1-naphthol-3,6,8-trisulfonic acid
1-naphthol-2-sulfonic acid
p-(ω-Benzoylacetamino) benzene sulfonic acid
2,4-di-nitrophenylacetic acid
1-amino-8-naphthol-2,4-disulfonic acid
1-naphthol-4,8-disulfonic acid
1-p-sulfophenyl-3-methyl-5-pyrazolone
1-phenyl-3-meta-sulfobenzamido-5-pyrazolone
1-naphthol-5-sulfonic acid

It will be noted that it is stated in U. S. Patents 2,445,252 and 2,480,815 that J-acid is not sufficiently stable to be of use in color processes employing bleaching or oxidizing baths, such as used in our invention for the removal of silver images during the processing of color films. For the purposes of this invention the stability of coupled dyes from J acid is of no consequence since this dye is soluble and does not remain in the final photographic image.

It will be apparent that our invention can be used in conjunction with many types of emulsion layers regardless of silver halide concentration, to effect contrast and grain favorably. While the faster and coarser grained emulsions of the concentration indicated are particularly adapted to use in our process, for some purposes the finer-grained emulsions can be used but the alteration in contrast and grain of the dye images obtained therefrom is less pronounced.

The invention is particularly applicable to use in conjunction with multilayer color films containing colored color-forming coupler compounds such as disclosed in U. S. Patents 2,428,054 and 2,449,966. Likewise, mixed grain photographic elements, such as described in U. S. Patents 2,490,749 and 2,490,751, are adapted to use in our process for the mentioned purposes by utilizing coupler-containing mixed grain emulsions having silver halide concentrations of the order indicated and developing such emulsions with color developer compositions containing diffusible coupler compounds such as illustrated.

If desired, the soluble couplers forming diffusible dyes such as mentioned can be used in color developing compositions also containing soluble coupler compounds forming substantially non-diffusible dyes. The non-diffusible dyes then remain in the photographic layer forming the color photographic image whereas the diffusible dye images formed along with them in color development leach out of the photographic layers in washing. For this purpose, the mentioned sulfonated naphthol types of couplers are more useful than couplers such as the simple mono and polyhydric phenols. Such developer compositions are particularly useful for the development of dye images in emulsion layers devoid of coupler compounds; however, the effect obtained may be somewhat different than the case when the diffusible coupler is in the de-

veloper and the non-diffusible coupler is in the emulsion.

A particular application of the process of our invention is to the production of monochrome fine grain dye images in processes normally employing only black-and-white materials and processing. For example, in processes in which a fine grain silver image is usually employed it was found that our process could be used to obtain the requisite fine grain image with a substantial increase in effective emulsion speed, or alternately a reduction in graininess without loss in effective emulsion speed. The process was carried out substantially as set forth in the above example employing the non-diffusing coupler or mixture of different non-diffusing couplers in the emulsion and the diffusing coupler in the color-developing solution, the silver image being removed from the emulsion following development leaving a fine grained dye image. Alternately, both the non-diffusing coupler and the diffusing coupler can be used in the developer which permits the use of conventional black-and-white sensitive materials.

What we claim is:

1. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, developing the exposed emulsion layer with a color-developing solution containing a mixture of a primary aromatic amino silver halide developing agent and a diffusible coupler compound, to obtain in the exposed region of the emulsion layer both a non-diffusible dye image from the non-diffusible coupler and a diffusible dye image from the diffusible coupler, and washing the diffusible dye image from the emulsion layer.

2. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible dye image, and washing the diffusible dye image from the emulsion layer.

3. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound and at least about 50 mg. of silver as silver halide per sq. ft. of emulsion, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible dye image, and washing the diffusible dye image from the emulsion layer.

4. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, and from about 50 to 750 mg. of silver as silver halide per sq. ft. of emulsion, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible dye image, and washing the diffusible dye image from the emulsion layer.

5. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound containing a phenolic hydroxyl group to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and containing a diffusible cyan dye image, and washing the diffusible cyan dye image from the emulsion layer.

6. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound containing a group of atoms having a reactive methylene group to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible dye image, and washing the diffusible dye image from the emulsion layer.

7. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound containing a 5-pyrazolone group to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible magenta dye image, and washing the diffusible magenta dye image from the emulsion layer.

8. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound containing a group of atoms having a —CO—CH_2—CO— group to

obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible yellow dye image, and washing the diffusible yellow dye image from the emulsion layer.

9. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound containing a naphthol sulfonic acid group to obtain in the exposed regions of the emulsion layer a non-diffusible dye image having the contrast of the process and a diffusible cyan dye image and washing the diffusible cyan dye image from the emulsion layer.

10. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient diffusible coupler compound of the class consisting of 1-naphthol-5-sulfonic acid, 1 - p - sulfophenyl-3-methyl-5-pyrazolone, 1 - phenyl-3-metasulfo-benzamido-5-pyrazolone, 1-amino-8-naphthol - 3,6 - disulfonic acid, 2-amino-5-naphthol-7-sulfonic acid, 1,8-dihydroxy-naphthalene disulfonic acid, 1-naphthol-3,6,8-trisulfonic acid, 1-naphthol-2-sulfonic acid, p-(ω-benzoylacetamino) benzene sulfonic acid, 1-amino-8-naphthol-2,4-disulfonic acid, 1-naphthol-4,8-disulfonic acid and 2,4-dinitrophenylacetic acid to obtain in the exposed regions of the emulsion layer a non-diffusing dye image having the contrast of the process and a diffusible dye image, and washing, the diffusible dye image from the emulsion layer.

11. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound, which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient 1-amino-8-naphthol-3,6-disulfonic acid to obtain in the exposed regions of the emulsion layer a non-diffusing dye image having the contrast of the process and a diffusible cyan dye image, and washing the diffusible dye image from the emulsion layer.

12. A process for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer containing a non-diffusing coupler compound which emulsion is developable with a solution of a primary aromatic amino silver halide developing agent to a contrast higher than that of the color process, developing the exposed emulsion layer with said color-developing solution containing a mixture of said developing agent and sufficient 1-naphthol-3,6,8-trisulfonic acid to obtain in the exposed regions of the emulsion layer a non-diffusing dye image having the contrast of the process and a diffusible cyan dye image, and washing the diffusible dye image from the emulsion layer.

13. The process of claim 17 in which the emulsion layer is contained in a multilayer color film.

14. The process of claim 11 in which the emulsion layer is contained in a multilayer color film.

15. The process of claim 12 in which the emulsion layer is contained in a multilayer color film.

16. A method for preparing colored photographic images which comprises exposing to a subject a light-sensitive silver halide emulsion layer, developing the exposed emulsion layer with a color-developing solution containing a primary aromatic amino silver halide developing agent, a coupler compound forming a non-diffusing dye image in the emulsion layer, and a coupler compound containing a sulfonated naphthol group forming a diffusible dye image in the emulsion layer, and washing the diffusible dye image from the emulsion layer.

17. A process for preparing a colored photographic image in an exposed silver halide emulsion layer containing a non-diffusing coupler compound, which comprises developing the exposed emulsion layer with a color-developing solution containing a mixture of a primary aromatic amino silver halide developing agent and a diffusible coupler compound, to obtain in the exposed region of the emulsion layer both a non-diffusible dye image from the non-diffusible coupler and a diffusible dye image from the diffusible coupler, and washing the diffusible dye image from the emulsion layer.

18. The process of claim 17 in which the exposed emulsion layer designated is an emulsion layer which has been exposed to a subject, developed by black-and-white development and reversal exposed.

No references cited.