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PRODUCTION OF SUBTRACTIVELY COLORED PHOTOGRAPHIC MATERIAL

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10 Claims. (Cl. 96—22)

The present invention relates to the production of subtractively colored photographic material, and more particularly to the production of such material by utilizing the sulfonhydrazide color development to form yellow and magenta azo dye images, and a further additional step to produce the cyan image. This is a division of our co-pending application Serial No. 206,938, filed January 19, 1951, now Patent No. 2,708,625, entitled "Production of Subtractive Color Images by Sulfonhydrazide Color Development Coupled With an Additional Step to Produce the Cyan Image."

United States Patent 2,424,256, granted July 22, 1947, to applicants, describes the production of azo dye images in photographic silver halide emulsion layers by color developing the exposed emulsion layers with a sulfonhydrazide color developer in the presence of a color former.

The patent points out that by selecting the appropriate color developer and color former combinations, it is possible to produce yellow, magneta and cyan azo dye images in monolayer material. However, experience has shown that it is difficult to find 3 color formers which would simultaneously combine with one and the same sulfonhydrazide color developer, to produce the 3 subtractive color images.

In the silver azo dye bleach-out process which is adapted for the manufacture of color prints, the problem of selecting the dyes is relatively simple for the reason that azo dyes of acceptable photographic characteristics are incorporated as such in the sensitized layers, and after exposure and black and white development the dyes are bleached in situ with the silver image. However, no one to date has synthesized a cyan azo dye color former for use in the silver azo dye bleach-out "taking film" process in which the azo dyes must be formed indiscriminately from one and the same diazonium salt and then bleached selectively after development of the sensitized material to silver images. In the latter case, the problem was only solved by using yellow and magenta azo dye color formers in combination with a heterocyclic color component which is capable of being selectively bleached at a silver image, and which is capable of forming a blue-green complex ferrous iron dye image. In the latter connection, reference is made to the co-pending application of Joseph A. Sprung, Serial No. 156,730, filed April 18, 1950, now Patent No. 2,635,960, and entitled "Hight Speed Silver Dye Bleach Out Taking and Printing Film."

It has been observed that the sulfonhydrazide color developer is particularly useful for producing yellow and magenta azo dye images which possess excellent fastness to light and chemicals, and whose spectral characteristics are highly desirable from the photographic color standpoint.

We have now found that capital can be made of this observation by the construction of a 2-step process in which the sulfonhydrazide color developer is employed

for producing the yellow and magenta azo dye images, and a separate step is resorted to for the formation of the cyan dye image. We have also constructed photographic material which is amenable to such processing, and such material and the processing thereof, as previously indicated, constitute the purposes and objects of our invention.

The light sensitive photographic color material which is designed for use with our method may be constructed in several fashions. Preferably, however, our material is constructed as follows:

A red sensitive silver halide emulsion containing a color former fast to diffusion and capable of yielding a quinonimine cyan dye image is cast on a base. Over the red sensitive emulsion there is cast a green sensitive emulsion containing a color former fast to diffusion and capable of yielding a magenta azo dye image with a sulfonhydrazide developer. Over the green sensitive emulsion there is cast a colloidal silver layer, and over this layer a blue sensitive emulsion containing a color former fast to diffusion and capable of yielding a yellow azo dye image upon development with a sulfonhydrazide developer.

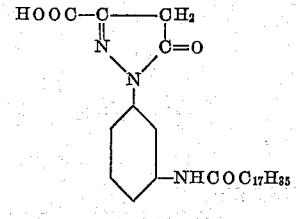
The color formers which are utilized for the formation of the yellow azo dye image are pyrazolones, preferably having a phenyl substituent in the 1-position, open chain ketomethylene compounds and phenols, said compounds containing a group rendering them fast to diffusion in a photographic silver halide emulsion. This end is best accomplished by employing as a substituent therein an aliphatic carbon chain having at least 10 carbon atoms.

Pyrazolones which are suitable for our purpose are described in U. S. P. 2,186,849, granted January 9, 1940, to Wilmanns et al., and U. S. P. 2,292,575, granted August 11, 1942, to Hans Loleit et al. Examples of such pyrazolones are, for example:

1-(5'-sulfo-3'-stearylaminophenyl)-3-methyl - 5 - pyrazolone;

1-(4'-stearylaminophenyl)-3-methyl-5-pyrazolone;

1-(3'-stearylaminophenyl)-5-pyrazolone-3-carboxylic acid of the formula:



and the like.

Examples of suitable open chain ketomethylene compounds are:

3'-stearylaminobenzoylacetanilide-4-carboxylic acid;

3'-myristylaminobenzoylacetanilide-4-carboxylic acid;

3-acetoacetylamino-6-N-methyl - N - octadecylamino-benzenesulfonic acid, and the like.

Examples of suitable phenols are:

2-hydroxy-4-(3'-stearylaminophenylsulfonamido) - benzenesulfonic acid;

2 - hydroxy-4-(3'-myristylaminophenylsulfonamido)-benzenesulfonic acid, and the like.

Color formers suitable for production of the magenta azo dye image are naphthols having a free position ortho or para to the coupling directing phenolic hydroxyl group and having a group rendering the naphthol fast to diffusion in photographic silver halide emulsions. As previously noted, this substituent generally takes the form of a long aliphatic chain.

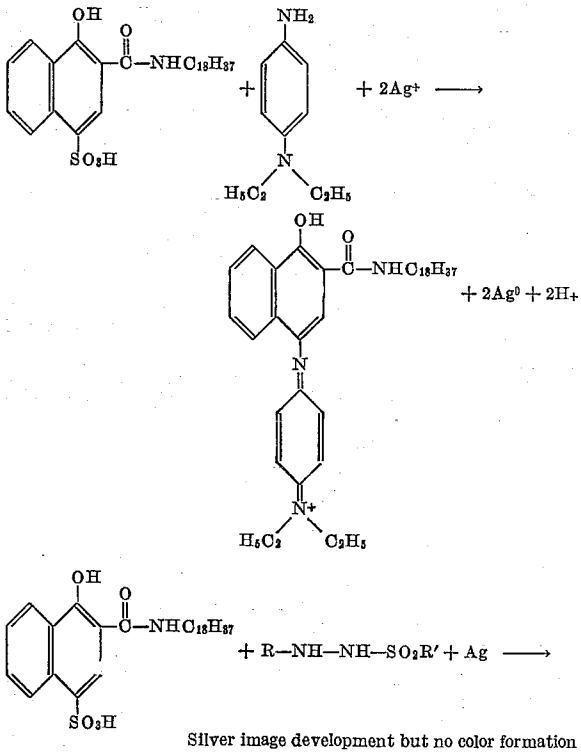
Naphthols suitable for our purpose are described in

U. S. P. 2,324,832, granted July 20, 1943, to Frohlich et al. Examples of such naphthols are:

1-hydroxy-2 - naphthoylamino-4' - methyloctadecylaminobenzene-3'-sulfonic acid;
1-hydroxy-2-naphthoylamino - 2' - methyloctadecylaminobenzene-5-sulfonic acid;
8-(3'-stearylaminobenzamido)-1-naphthol - 3,6 - disulfonic acid, and the like.

The color former for producing the cyan dye image is a compound containing a phenolic hydroxyl group and bearing a substituent rendering it fast to diffusion in photographic silver halide emulsions and in para position to the phenolic hydroxyl group, a replaceable substituent such as bromine or a sulfonic acid group. Such color formers may be phenols, naphthols or 8-hydroxyquinolines.

It has been observed, and this is an important feature of our invention, that such color formers are not affected by sulfonhydrazide color development due to the fact that the coupling position is blocked by the bromine or sulfonic acid group. Such group on the other hand is displaced by the conventional developers for producing quinonimine dye images such as developers of the p-phenylenediamine type. This fact is represented by the following equations, the first of which discloses the development with p-diethylaminoaniline and the second with a sulfonhydrazide.



Silver image development but no color formation

R=a phenyl radical such as methoxyphenyl
R'=an alkyl radical such as methyl, or aryl, such as phenyl.

Color formers capable of yielding the cyan dye images upon color development with a developer of the p-phenylenediamine type are, for instance, the phenols and naphthols described in U. S. Patent 2,343,051, granted February 29, 1944 to Alfred Frohlich. Examples of such color formers are:

1,2,3-xylenolcarboxyloctadecylarmino-4-sulfonic acid;
2-(3'-octadecylamino-4'-sulfophenylcarbamyl) - 1 - naphthol-4-sulfonic acid;
2-(3'-octadecylamino-4'-carboxyphenylcarbamyl)-1-naphthol-4-sulfonic acid;
2-(octadecylcarbamyl)-1-naphthol-4-sulfonic acid, and the like.

A multilayer film of the above construction may be processed to give reversed dye images according to the following schemes:

SCHEME 1

The tripack is exposed and developed to primary silver images in a black and white developer. The residual silver halide is then re-exposed to white light and the blue and green sensitive layers are color developed to yield yellow and magenta azo dye images by means of a sulfonhydrazide developer. The red sensitive layer is then developed with a p-phenylenediamine developer to yield a cyan quinoneimine dye image in the red sensitive layer.

SCHEME 2

The tripack is exposed and developed to primary silver images in a black and white developer. The red sensitive layer is then re-exposed to red light from the back and is color developed with a p-phenylenediamine type developer. The residual silver halide of the blue and green sensitive layers is then re-exposed to white light and these two layers are developed with a sulfonhydrazide developer.

Either of these procedures, as is evident, will produce the subtractive colored images in the three layers.

It is, of course, apparent to operators skilled in this art that certain precautions are necessary in order to obtain, with the above procedures, a well balanced set of subtractive colored images. These precatuions, moreover, may be exercised either with respect to the tripack or with respect to the chemicals utilized in the processing of the tripack.

For example, in Scheme 1 above, it is not of too much importance if the sulfonhydrazide developer penetrates to the bottom red sensitive layer because it cannot develop color with the quinoneimine color former located therein. However, care must be taken that it does not totally develop the reversed silver halide image in the bottom layer or sufficient silver halide will not be available to give the cyan quinoneimine dye image of the necessary density and contrast during the second development.

It is, therefore, important to restrict the penetration of the sulfonhydrazide developer to the bottom layer and this end can be accomplished either (1) by adding gelatin anti-swelling reagents such as sodium sulfate to the sulfonhydrazide developer, and/or (2) by locating a relatively thick gelatin layer between the green and red sensitive silver halide emulsion layers.

Furthermore, after the sulfonhydrazide development, it is essential that no residual silver halide remain in the blue and green sensitive layers. In this connection, it is to be pointed out that the color formers located in these layers will couple with the oxidation products of a p-phenylenediamine developer to yield magenta images (with the pyrazolones) and cyan images (with the phenols or naphthols). Consequently, if any silver halide remains after the color development step in the blue and green sensitive layers, color degradation will necessarily ensue.

Various means are available for remedying this situation. One of these involves the addition of mild silver halide solvents such as ethylenediamine to the sulfonhydrazide developer compositions to insure complete removal of all the residual silver halide in the blue and green sensitive layers.

Alternately, we may resort to controlled bathing of the tripack prior to quinoneimine color development in a solution of insoluble silver salt forming substances such as potassium iodide or the 2-thiobarbituric acid derivatives or thioureido naphthols described in U. S. Patent 2,636,821, issued April 28, 1953, to Donald E. Sargent, entitled "Process of Rendering Undevelopable the Silver Halides Present in an Outer Layer of Multi-Layer Color Film." This controlled bathing will block or render undevelopable the residual silver halide in the two top layers of the tripack.

It has been indicated above that it is preferred to con-

struct the tripack with the color formers located in a non-diffusing state in the various sensitized layers. It is obvious, however, that the color formers may be incorporated in the developing solutions and the tripack processed according to the selective second exposure and color development method as described for instance in U. S. Patent 2,320,418, granted June 1, 1943, to Eggert et al. and in U. S. Patent 2,191,502, granted February 27, 1940, to Sease et al.

It is apparent that in this processing the same developers and color formers would be used, excepting that the color formers would not contain the group rendering them fast to diffusion in the emulsions. In the latter case, it would not be important to select a cyan quinoneimine color former with a blocking substituent in the para position to the activating group because the excess color former would necessarily be removed by diffusion during the washing process following the quinoneimine color forming step, and would not be present either during a preliminary or subsequent sulfonhydrazide development.

It will be evident to a skilled operator that one may use conjointly diffusing and non-diffusing color formers to effect color formation in the same film. For example, one may use non-diffusing yellow and magenta color formers (developable by a sulfonhydrazide developer) and a diffusing cyan color former (developable with a diffusing p-phenylenediamine developer).

It has been indicated above that the usual arrangement of the sensitive layers in the tripack is to be preferred. However, it is possible by reversing the order of the coatings, to process the film from the standpoint of the production of the cyan image by means other than described. In reversing the order of the coatings, the blue sensitive layer would be coated on the base, the green sensitive on the blue sensitive layer, and the red sensitive layer would be outermost.

In this case, the red sensitive emulsion, being on the top layer of the tripack, lends itself to the formation therein of a surface cyan dye image by any of the following methods:

(1) Imagewise mordanting of the silver halide according to British Patent 466,710, and subsequent dyeing of the mordant image with cyan basic dyestuffs, such as Methylene Blue or Rhoduline Blue 6GA.

(2) Conversion of the silver image to cyan Prussian Blue image according to U. S. Patents 2,320,108 and 2,320,109.

(3) Conversion of the silver image to a silver ferricyanide image, according to U. S. Patent 1,279,248, and the subsequent use of the latter to oxidize in an imagewise manner the sulfuric acid esters of the leuco forms of the cyan vat dyes.

(4) Conversion of the silver halide image to a metallic complex salt image by bathing the film in a solution of a cyan ferrous complex salt of 5-nitroso-2-thiobarbituric acid, as described, for example, in U. S. Patents 2,533,181 and 2,533,182.

The sulfonhydrazide developers which are to be employed are those described in U. S. Patent 2,424,256 granted to Willy A. Schmidt and Joseph A. Sprung on July 22, 1947.

Examples of such sulfonhydrazide developers are:

β-(2-ethoxyphenyl)-methanesulfonhydrazide;
β-(3'-methoxyphenyl)-methanesulfonhydrazide;
β-phenyl-3-carboxybenzenesulfonhydrazide;
β-(3'-acetamidophenyl)-methanesulfonhydrazide, and the like.

The developers for production of the quinoneimine dye images are the conventional p-phenylenediamine developers such as p-phenylenediamine itself, p-diethylaminoaniline, p-dimethylaminoaniline, and the like.

The invention is illustrated by the following examples but it is to be understood that the invention is not restricted thereto. The parts are by weight unless otherwise stated.

PREPARATION OF TRIPACK

Example I

Onto a transparent base there is cast a red sensitive silver bromide emulsion containing per kilo of emulsion, 20 grams of 2-(octadecylcarbamyl)-1-naphthol-4-sulfonic acid (prepared according to Fiat Final Report #943, page 68). Over the red sensitive layer there is cast a gelatin separation layer, and over the gelatin separation layer a green sensitive silver bromide emulsion containing per kilo, 20 grams of 8-(3'-stearoylaminobenzamido)-1-naphthol-3,6-disulfonic acid. Over the green sensitive layer there is cast a yellow colloidal silver filter layer, and over this layer there is cast a blue sensitive silver bromide emulsion containing per kilo, 20 grams of 1-(3'-stearylaminophenyl)-5-pyrazolone-3-carboxylic acid.

Example II

The procedure is the same as in Example I, excepting that the azo color former in the green sensitive layer is replaced by the compound 1-hydroxy-2-naphtholyamino-2'-methyloctadecylaminobenzene-5-sulfonic acid (prepared according to Fiat Final Report #943, page 68).

PREPARATION OF COLOR FORMING COMPONENTS

Example III.—β-(2-ethoxyphenyl)-methanesulfonhydrazide

A mixture of 37 grams (0.2 mol) of 2-ethoxyphenylhydrazine hydrochloride, 22.9 grams (0.2 mol) of methanesulfonylchloride and 33.6 grams (0.4 mol) of sodium bicarbonate in 400 cc. of ethyl ether, was stirred for 1 hour at room temperature and finally refluxed for 2 hours on a steam bath. The cooled mixture was treated with 400 cc. of low boiling petroleum ether, and the precipitated material was removed by filtration and washed with petroleum ether. The solid was digested twice at room temperature with dilute hydrochloric acid (5 cc. of hydrochloride acid in 250 cc. of water), and was finally washed with water and air dried. (Yield: 40 grams—87%, M. P. —105° C.)

Example IV.—1-(3'-stearylaminophenyl)-5-pyrazolone-3-carboxylic acid

A well agitated warm (steam bath) solution of 53.7 parts of 1-(3-aminophenyl)-5-pyrazolone-3-carboxylic acid in 114 parts of pyridine and 336 parts of dimethylformamide was treated with 89 parts of freshly prepared stearoylchloride over a period of 1½ hours. The solution was heated on a steam bath until the diazotization test for free amino group was negative. The reaction mixture was poured into a solution of 128 parts of concentrated HCl in 2000 parts of water, and the precipitate was removed by filtration and washed with water. After the compound had been dried in an oven at 50° C., it was extracted in a Soxhlet apparatus with high boiling petroleum ether to remove the stearic acid. The extracted solid was dissolved in a minimum amount of boiling pyridine, decolorized with "Norite," and was treated with hot glacial acetic acid (approximately three times the volume of pyridine) to incipient cloudiness. The precipitated color former, which was removed by filtration from the cooled (50° C.) solution, was washed with cold 95% ethanol and air dried. The yield was 75.5 parts.

Example V.—8-(3'-stearylaminobenzamido)-1-naphthol-3,6-disulfonic acid

To a solution of 92 parts of finely powdered 8-(3'-aminobenzamido)-1-naphthol-3,6-disulfonic acid in 400 parts of dimethylformamide and 100 parts of pyridine there was slowly added 61 parts of freshly prepared stearoyl chloride. The mixture was heated on a steam bath for 30 minutes and then additional stearoyl chloride

was added until a diazotization test showed the amino group to be completely acylated. The reaction mixture was poured into 2000 parts of 15% sodium chloride solution and 100 parts of concentrated HCl. After a period of 15 minutes, the precipitate was removed by filtration, digested with 2000 parts of 15% sodium chloride solution and was again removed by filtration. The filter cake was dried in vacuo at 50° C. The dried finely powdered solid was extracted once with boiling acetone and twice with low boiling petroleum ether. Sodium chloride was eliminated by an extraction of the production with dimethylformamide. The solvent was removed by vacuum distillation and the residue, which was digested with acetone, weighed 109.5 parts.

PROCESSING OF MULTILAYER FILM

Example VI

The tripack of Example I is exposed and then processed as follows:

Step 1—Primary silver image development, 12 minutes at 20° C.:

Water	cc..	750.0
Metol	grams..	3.0
Sodium sulfite (anhydrous)	do....	50.0
Sodium carbonate (monohydrate)	do....	40.0
Sodium thiocyanate	do....	2.0
Potassium bromide	do....	2.0

Water to make 1000.0 cc.

Step 2—Short stop for 3 minutes.

Sodium bisulfite	grams..	50.0

Water to make 1000.0 cc.

Step 3—Wash for 5 minutes.

Step 4—Overall white light exposure.

Step 5—Azo dye color development, 5 to 10 minutes at 20° C.:

β-(2-ethoxyphenyl) - methanesulfonhydrazide in 15.0 cc. dioxane	grams..	3.0
Potassium bromide	do....	2.0
Sodium sulfite (anhydrous)	do....	10.0
Sodium carbonate (monohydrate)	do....	25.0
Ethylenediamine	cc..	20.0
Hydroxylamine hydrochloride	grams..	2.0

Water to make 1000.0 cc.

Step 6—Short stop for 3 minutes.

Sodium bisulfite	grams..	50.0

Water to make 1000.0 cc.

Step 7—Wash for 10 minutes.

Step 8—Quinoneimine color development, 18 minutes:

Water	cc..	750.0
Sodium bisulfite	grams..	1.0
p-Diethylaminoaniline hydrochloride	do....	3.0
Sodium carbonate (anhydrous)	do....	67.5
Potassium bromide	do....	2.5

Water to make 1000.0 cc.

Step 9—Short stop for 2 minutes.

Sodium bisulfite	grams..	50.0

Water to make 1000.0 cc.

Step 10—Harden for 4 minutes at 20° C.

Water	cc..	1000.0
Potassium chrome alum	grams..	30.0

Step 11—Wash for 10 minutes.

Step 12—Bleach for 5 minutes at 20° C.

Water	cc..	750.0
Potassium ferricyanide	grams..	60.0
Potassium bromide	do....	15.0
Dibasic sodium phosphate	do....	13.0
Sodium bisulfate	do....	6.0

Water to make 1000.0 cc.

Step 13—Wash for 3 minutes.

Step 14—Fix for 5 minutes at 20° C.

Water	cc..	1000.0
Sodium thiosulfate	grams..	200.0

Step 15—Wash.

There is thus obtained subtractively colored, brilliant reversed dye images.

Example VII

The film of Example II is exposed and then processed as follows:

Step 1—Primary silver image development, 12 minutes at 20° C.:

Water	cc..	750.0
Metol	grams..	3.0
Sodium sulfite (anhydrous)	do....	50.0
Sodium carbonate (monohydrate)	do....	40.0
Sodium thiocyanate	do....	2.0
Potassium bromide	do....	2.0

Water to make 1000.0 cc.

Step 2—Short stop for 3 minutes.

Sodium bisulfite	grams..	50.0

Water to make 1000.0 cc.

Step 3—Wash for 5 minutes.

Step 4—Selective re-exposure to red light through film back.

Step 5—Quinoneimine color development, 15 minutes at 20° C.:

Water	cc..	750.0
p-Diethylaminoaniline hydrochloride	grams..	2.75
Hydroxylamine hydrochloride	do....	1.2
Sodium sulfite (anhydrous)	do....	2.0
Sodium carbonate (monohydrate)	do....	66.0
Potassium bromide	do....	2.5

Water to make 1000.0 cc.

Step 6—Short stop for 1 minute.

Sodium bisulfite	grams..	50.0

Water to make 1000.0 cc.

Step 7—Harden for 4 minutes.

Water	cc..	1000.0
Potassium chrome alum	grams..	30.0

Step 8—Wash for 10 minutes.

Step 9—Re-exposure to white light.

Step 10—Azo dye color development, 5 to 10 minutes at 20° C.:

	Grams
β-(2-ethoxyphenyl)methane sulfonhydrazide in 15.0 cc. of dioxane	3.0
Potassium bromide	2.0
Sodium sulfite (anhydrous)	10.0
Sodium carbonate (monohydrate)	25.0
Ethylenediamine	20.0
Hydroxylamine hydrochloride	2.0

Water to make 1000.0 cc.

Step 11—Short stop for 3 minutes.

Step 12—Wash for 10 minutes.

Step 13—Bleach for 5 minutes.

Water	cc..	750.0
Potassium ferricyanide	grams..	60.0
Potassium bromide	do....	15.0
Dibasic sodium phosphate	do....	13.0
Sodium bisulfate	do....	6.0

Water to make 1000.0 cc.

Step 14—Wash for 3 minutes.

Step 15—Fix for 5 minutes.

Water	cc..	1000.0
Sodium thiosulfate	grams..	200.0

Step 16—Wash.

The result is substantially the same as that of Example I.

Various modifications of the invention will occur to persons skilled in the art. Thus, as is evident, we may use other color formers of the type previously mentioned in lieu of those of the examples. Similarly, any of the sulfonhydrazides contemplated in U. S. P. 2,424,256 may be employed. We, therefore, do not intend to be limited

in the art granted, except as necessitated by the appended claims.

We claim:

1. The process of producing subtractively colored images in a photographic color tripack comprising a base, a red sensitive silver halide emulsion on the base containing a color former capable of reacting with the oxidation products of a primary aromatic amino developer to produce a cyan dye, said color former containing a phenolic hydroxyl group and having a group rendering the color former non-migratory in the silver halide emulsion and being substituted para to the phenolic hydroxyl group by a substituent which is replaceable on development with a primary aromatic amino developer but which renders the color former incapable of reacting with the oxidation products of a β-aromatic sulfonhydrazide developer, a green sensitive silver halide emulsion on the red sensitive emulsion containing a magenta azo color former capable of reacting with the oxidation products of a primary aromatic amino developer, said color former bearing a group rendering it non-migratory in the emulsion and having a free coupling position selected from the class ortho and para to the coupling directing group, and a blue sensitive silver halide emulsion on the green sensitive emulsion containing a yellow azo color former capable of reacting with the oxidation products of a primary aromatic amino developer and having a group rendering it non-migratory in the emulsion, which comprises exposing said tripack, developing it in a black and white developer, re-exposing the tripack to white light, color developing the blue and green sensitive layers only with a β-aromatic sulfonhydrazide developer and subsequently color developing the red sensitive layer with a primary aromatic amino developer.

2. The process as defined in claim 1 including the step of retarding penetration of the sulfonhydrazide developer to the red sensitive layer.

3. The process as defined in claim 1 including the step of retarding penetration of the sulfonhydrazide developer to the red sensitive layer by adding gelatin anti-swelling reagents to the sulfonhydrazide developer.

4. The process as defined in claim 1, in which the sulfonhydrazide development step is followed by a treatment of the blue and green sensitive layers to render the residual silver halide therein non-developable.

5. The process of producing subtractively colored images in a photographic color tripack comprising a base, a red sensitive silver halide emulsion on the base containing a color former capable of reacting with the oxidation products of a primary aromatic amino developer to produce a cyan dye, said color former containing a phenolic hydroxyl group and having a group rendering the color former non-migratory in the silver halide emulsion and being substituted para to the phenolic hydroxyl group by a substituent which is replaceable on development with a primary aromatic amino developer but which renders the color former incapable of reacting with the oxidation products of a β-aromatic sulfonhydrazide developer, a green sensitive silver halide emulsion on the red sensitive emulsion containing a magenta azo color former capable of reacting with the oxidation products of a primary aromatic amino developer, said color former bearing a group rendering it non-migratory in the emulsion and having a free coupling position selected from the class ortho and para to the coupling directing group, and a blue sensitive silver halide emulsion on the green sensitive emulsion containing a yellow azo color former capable of reacting with the oxidation products of a primary aromatic amino developer and having a group rendering it non-migratory in the emulsion, which comprises exposing said tripack, developing it in a black and white developer, selectively re-exposing the red sensitive layer, color developing the same with a primary aromatic amino developer, re-exposing the tripack to white light and color developing the blue and green sensitive layers with a β-aromatic sulfonhydrazide developer.

6. The process of producing subtractively colored images on a photographic colored tripack comprising a base, a red sensitive silver halide emulsion on the base containing a color former capable of reacting with the oxidation products of a primary aromatic amino developer to produce a cyan dye, said color former containing a phenolic hydroxyl group and having a group rendering the color former non-migratory in the silver halide emulsion and being substituted para to the phenolic hydroxyl group by a substituent which is replaceable on development with a primary aromatic amino developer but which renders the color former incapable of reacting with the oxidation products of a β-aromatic sulfonhydrazide developer, a green sensitive silver halide emulsion on the red sensitive emulsion containing a magenta azo color former capable of reacting with the oxidation products of a primary aromatic amino developer, said color former bearing a group rendering it non-migratory in the emulsion and having a free coupling position selected from the class ortho and para to the coupling directing group and a blue sensitive silver halide emulsion on the green sensitive emulsion containing a yellow azo color former capable of reacting with the oxidation products of a primary aromatic amino developer and having a group rendering it non-migratory in the emulsion, which comprises exposing said tripack, color developing the blue and green sensitive layers only with a β-aromatic sulfonhydrazide developer and color developing the red sensitive layer with a primary aromatic amino developer.

7. The process as defined in claim 6 wherein the color development of the red sensitive layer precedes the color development of the blue and green sensitive layers.

8. The process as defined in claim 6 wherein the cyan color former is selected from the class consisting of phenols and naphthols, the magenta color former is a naphthol and the yellow color former is selected from the class consisting of pyrazolones, open chain keto methylene compounds and phenols.

9. The process as defined in claim 1 wherein the cyan color former is selected from the class consisting of phenols and naphthols, the magenta color former is a naphthol and the yellow color former is selected from the class consisting of pyrazolones, open chain keto methylene compounds and phenols.

10. The process as defined in claim 5 wherein the cyan color former is selected from the class consisting of phenols and naphthols, the magenta color former is a naphthol and the yellow color former is selected from the class consisting of pyrazolones, open chain keto methylene compounds and phenols.

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