

1

2

METHOD FOR PROCESSING MULTILAYER COLOR FILM

Philip E. Perkins and Herbert L. Rees, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
No Drawing. Filed Nov. 14, 1963, Ser. No. 323,586
21 Claims. (Cl. 96—22)

This invention relates to a method for reversal processing of multilayer color films of the reversal type containing silver halide emulsion layers sensitive to different spectral regions and which are reversal exposed and developed with color developing solutions containing color coupled compounds.

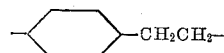
Color films of the reversal type employed in the process of the present invention usually carry at least three silver halide emulsion layers sensitive to different regions of the spectrum. Frequently the uppermost layer is blue-sensitive, the next layer is green-sensitive, while the emulsion layer adjacent to the support is red-sensitive. Between the blue-sensitive and green-sensitive layers there is generally a filter layer for absorbing blue radiation which may be transmitted through the blue-sensitive layer. The multilayer element can also have other interlayers for specialized purposes. Such multilayer color materials have been previously described in the prior art, such as Mannes et al., U.S. Patent 2,252,718, issued August 19, 1941. After exposure to a colored subject these films are usually processed by developing the film in a black-and-white developing solution to produce negative silver images in the emulsion layers, the red-sensitive emulsion layer is then reversal exposed and developed in a color-forming developer composition containing a cyan color forming coupler and a p-phenylenediamine silver halide developing agent whose oxidation product is reactive with a coupler to form a cyan dye image, the blue-sensitive emulsion layer is then reversal exposed and developed in a color developer containing a yellow color forming coupler to develop a yellow dye image in the layer, following which the middle green sensitive emulsion layer may be reversal exposed and developed with a color developing solution containing a magenta color forming coupler, or the reversal exposure of the green sensitive emulsion layer may be dispensed with and instead of fogging magenta color developer can be used for forming the magenta image in the green sensitive emulsion layer.

In processing reversal color films in this manner it is difficult to prevent dye images of the wrong color being developed in the emulsion layers. Thus, if the exposure of the silver halide in the blue sensitive emulsion layer has not been adequate, magenta dye can be subsequently developed in the layer which should contain only a yellow dye image. Accordingly, it has been a common practice, following development of the yellow dye image, to employ a black-and-white auxiliary developer which develops any residual silver halide in the blue sensitive emulsion layer. Such an auxiliary developing solution formulated so that it will not excessively fog the still undeveloped silver halide in the middle (magenta) layer will usually not complete development of the top layer unless all the silver halide grains in that layer have been made developable by adequate exposure to blue light during the reversal print step before the yellow color development step. Because of inadequate protection of the middle layer by the yellow filter layer it is often impossible to fully expose the top layer with blue light without also exposing some of the silver halide grains in the middle layer. If some middle-layer grains are

exposed to blue light before yellow color development, they will be developed in the yellow color developer giving yellow dye contamination in the middle layer. Accordingly, several problems can arise i.e., if the reversal exposure of the blue sensitive emulsion layer is not adequate to fully expose the layer this will lead to the formation of magenta dye in the layer. Also, blue light which fully exposes the blue sensitive emulsion layer may also expose some inherently blue light sensitive grains in the middle emulsion layer which is primarily sensitive to green light with the result that yellow dye will be formed in that layer. Furthermore it is often difficult to formulate a yellow color developer composition which will fully develop the top layer without giving excessive fog in the middle green sensitive emulsion layer, and when using a low fogging yellow color developer a black-and-white yellow auxiliary developer often must be used to complete development of the top layer and this may also fog the middle layer.

We have discovered that the mentioned problems can be solved by use of a combined auxiliary developer and reversal bath following color development of the blue sensitive emulsion layer and prior to color development of an adjacent emulsion layer such as the middle green sensitive emulsion layer of a conventional color film.

The combined auxiliary developer and reversal bath of the invention is an alkaline solution of a hydroquinone derivative and a boron compound nucleating agent for silver halide. The hydroquinone derivatives useful in the solution are those soluble in alkaline solution and containing a chain of at least 4 carbon atoms. The higher molecular weight hydroquinone derivatives should also contain solubilizing groups such as sulfo and carboxyl groups to increase the solubility of the compound in alkaline solution. The carbon chain of at least 4 carbon atoms may include the carbon atoms of a cyclic radical for example, as present in the 6-carbon atom chain of the radical



of compounds 10' and 11 below.

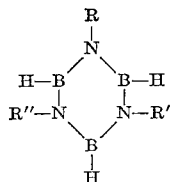
The boron compound nucleating agents for silver halide include boron compounds containing at least one hydrogen to boron bond. Thus, the boron compounds include the boranes and borazines. Included among the boron compounds are boranes such as the alkali metal borohydrides e.g., potassium and sodium borohydrides (KBH_4 and NaBH_4); the amine boranes having the formula



in which Z represents ammonia, an amine, such as an aliphatic amine, for example, methylamine, dimethylamine, trimethylamine, ethylamine, ethanolamine, diethylamine, triethylamine, diethanolamine, propylamine, 3-hydroxypropylamine, dipropylamine, tripropylamine, primary-butylamine, secondary-butylamine, tertiary-butylamine, primary-amylamine, secondary-amylamine, tertiary-amylamine, etc., a polyamine, for example, ethylenediamine, 2-aminoethylamine borane, etc., an aromatic amine, for example, aniline, etc., a cyclic amine for example pyridine, 2,6-lutidine, 3,4-lutidine, 2,4-lutidine, 2-ethylpyridine, 2,4-diethylpyridine, 2,6-diethylpyridine, 3,4-diethylpyridine, 2-propylpyridine, 4-propylpyridine, 3-propylpyridine, etc., boranes containing a hydrazine, a phosphine such as an alkylphosphine, for example, methylphosphine, dimethylphosphine, trimethylphosphine, ethylphosphine, diethylphosphine, triethylphosphine, propylphosphine, dipropylphosphine, tripropylphosphine, primary-butylphosphine, secondary-butylphosphine, etc., an

3

aryl phosphine, for example, phenylphosphine, etc., an arsine, such as an alkylarsine, for example, methylarsine, dimethylarsine, trimethylarsine, propylarsine, primary-butylarsine, secondary-butylarsine, amylarsine, etc., an arylarsine, for example, phenylarsine, etc., a stibine, such as an alkylstibine, for example, methylstibine, dimethylstibine, trimethylstibine, ethylstibine, diethylstibine, triethylstibine, propylstibine, primary-butylstibine, secondary-butylstibine, tertiary-butylstibine, etc., an arylstibine, for example, phenylstibine; and borazine nucleating agents of the formula:



wherein R, R' and R'' each represent a hydrogen atom, a halogen atom, such as chlorine, bromine, fluorine, iodine, an alkyl group, preferably lower alkyl, such as methyl, ethyl, propyl, butyl, etc., an alkoxy group, preferably lower alkoxy, such as methoxy, ethoxy, propoxy, butoxy, etc.,

Included among the boron compound nucleating agents of the invention are the following typical examples which are illustrative and not intended to limit the invention:

Alkali metal borohydrides:

Potassium borohydride
Sodium borohydride

Amine boranes:

Trimethylamine borane
Diethylamine borane
Triethylamine borane
Tert.-butylamine borane
Pyridine borane
2,6-lutidine borane

Polyamine boranes:

Ethylenediamine diborane
Hydrazine diborane

Phosphine borane:

Dimethylphosphine borane

Arsine borane:

Dimethylarsine borane

Stibine borane:

Dimethylstibine borane

Borazines:

Borazine
N,N',N''-Trimethyl borazine
N,N',N''-Trimethoxy borazine

These compounds and their preparations have been described in the literature. For example, the monograph, "Borax to Boranes," edited by T. Wartik, and Heinrich Noth Hassobeyer, Berichte, vol. 93, pages 928-38 and 1078-83 (1960), describe the aliphatic amine boranes. The pyridine and lutidine boranes are commercially available from the Callery Chemical Company, in Pittsburgh, Pennsylvania.

The phosphine boranes, the arsine boranes and stibine boranes are described in Miller et al. U.S. Patent 2,999,864, issued September 12, 1961.

The borazines are synthesized by condensation of diborane with the appropriate nitrogen compound. For example, borazine is made by condensing diborane with ammonia. N,N',N''-trialkyl borazine is produced by condensing diborane with the corresponding N-alkyl amine. An N,N'-dialkyl borazine is produced by condensing diborane with a mixture of ammonia and the appropriate N-alkylamine.

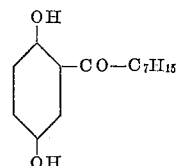
When the combined developer and reversal bath is used in a typical case for processing film of the reversal type, following color development of the blue sensitive emul-

4

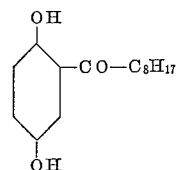
sion layer and prior to the last color development step, any residual undeveloped silver halide in the blue sensitive emulsion layer is thereby nucleated and reduced to silver without development of the silver in the adjacent green sensitive emulsion layer. However, the bath is also effective to nucleate the silver halide of the green sensitive emulsion layer without developing the silver halide thereof with the result that subsequently a conventional fogging or non-fogging color developer containing a magenta color forming coupler can be used. Accordingly, in the reversal exposure of the blue sensitive emulsion layer it is not necessary to completely expose the silver halide with the concomitant effect that there is less danger of exposing the adjacent green sensitive layer which is inherently sensitive to blue light.

The hydroquinone derivatives useful in a combined developer and reversal bath are those which are soluble in alkaline solution and containing a chain of at least 4 carbon atoms such as present in the following compounds. Included among the hydroquinones are the alkali soluble alkyl hydroquinones, the alkyl group of which contains at least 4 carbon atoms, preferably 4 to 20 carbon atoms. The 2,5-dihydroxyacyclopheones containing 8-10 carbon atom acyl groups, as in compounds 5, 6 and 7 below, are very useful.

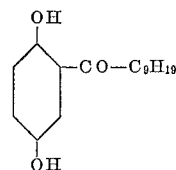
- (1) t-Butyl hydroquinone
- (2) n-Hexyl hydroquinone
- (3) n-Octyl hydroquinone
- (4) n-Nonyl hydroquinone
- (5) 2,5-dihydroxy-n-octanophenone



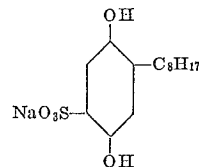
- (6) 2,5-dihydroxy-n-nonanophenone



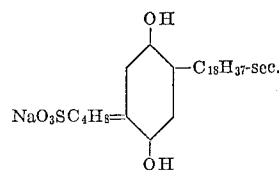
- (7) 2,5-dihydroxy-n-decanophenone



- (8) 2-n-octylhydroquinone-5-sulfonic acid, sodium salt

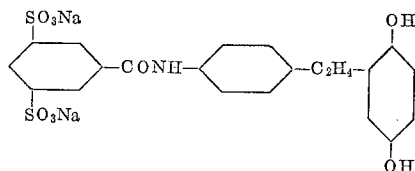


- (9) 2-(sec-octadecyl) - 5(sulfo-t-butyl) hydroquinone, sodium salt, dihydrate

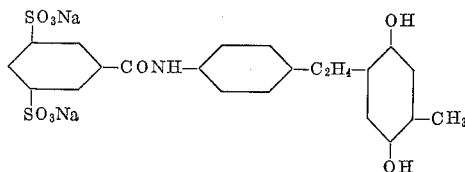


5

(10) 2-[4-(3,5-disulfo, benzamido)] phenethyl hydroquinone, disodium salt, dihydrate



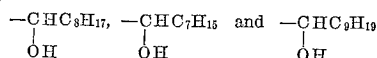
(11) 5-[4-(3,5-disulfo, benzamido)] phenethyl-2-methyl hydroquinone, disodium salt



These compounds are characterized by having good solubility in alkaline solution and possess the desired diffusibility through photographic emulsion layers such as gelatin silver halide emulsion layers. Accordingly the compounds are effective to limit the reduction of silver halide to a single emulsion layer such as the outer blue sensitive emulsion layer of a conventional multilayer color film. Alkaline solutions containing the boron compounds and the hydroquinone derivatives described above, and the use of the solutions in color processes as described herein, comprise preferred embodiments of our invention.

It should be noted that similar hydroquinone derivatives such as n-propyl hydroquinone are not useful in the process of the invention because they tend to cause development of the green sensitive emulsion layer to take place at the time the residual blue sensitive silver halide of the blue sensitive layer is being developed. Also the hydroquinone derivatives 2,5-di-t-butylhydroquinone, n-decylhydroquinone, laurylhydroquinone, cyclohexylhydroquinone and 2,5-di-cyclohexylhydroquinone are not useful in the process particularly because of low solubility in the borohydride solution. It should be particularly noted that while the 2,5-dihydroxyacylohydroquinones such as 6, 7 and 8 above e.g. 2,5-di-hydroxynonanophenone are very useful, the homologous compound 2,5-di-hydroxydodecanophenone is not useful in the process of the invention.

It is believed that when these latter compounds are used in the reversal bath, in the presence of the borohydride compound they are reduced to the corresponding alcohols. Thus, the groups $\text{—COC}_8\text{H}_{17}$, $\text{—COC}_7\text{H}_{15}$ and $\text{—COC}_9\text{H}_{19}$ of these compounds are reduced to



groups respectively. It is not known in which form the compounds are effective in the processes of the invention and it is to be understood that our invention includes compositions containing either form of the compounds in conjunction with the boron compounds, and the process of using either form of the compounds in the processing of color films as described herein.

The alkaline solutions containing the effective hydroquinone derivatives and boron compounds should be strongly alkaline having a pH of at least 10. About 0.05 gram to about 10 grams or more of the boron compounds may be used and from about 0.05 to 5.0 grams or more of the hydroquinone derivative per liter of solution. However, the quantity of boron compound and hydroquinone derivative used will depend in part upon the activity of these materials. In general too high a concentration may be expected to cause unwanted development of

6

the green sensitive (inner) emulsion layer during treatment of the blue sensitive (outer) emulsion layer with the alkaline solutions of boron compounds and hydroquinone derivative. The time of treatment of the films with the alkaline solutions of the invention can vary from about 15 to 120 seconds depending in part upon the temperature, concentration and type of boron and hydroquinone compounds used. Treatment of the films for too long can be expected to cause loss of dye image (magenta) in the inner emulsion layer or too short a treatment with the alkaline solutions can cause development of magenta dye in the outer emulsion layer where only yellow dye should be developed. The alkaline component of the solution may be strong organic or inorganic alkali such as alkali metal hydroxide and quaternary ammonium hydroxide. Other addenda commonly used in photographic developer compositions may be added.

The photographic elements to which our invention may be applied are those containing at least two silver halide emulsion layers, preferably gelatin silver halide emulsion layers, primarily sensitive to different spectral regions. In a preferred embodiment one emulsion layer is blue sensitive and the other emulsion layer or layers are green or red light sensitive. The blue sensitive emulsion layer is preferably the outermost layer. Thus, as mentioned above, the reversal exposure of the blue sensitive emulsion layer is not especially critical so long as the other layer or layers are not exposed at the same time. The boron compound-hydroquinone derivative compositions can be used in those cases where a red or green light sensitive emulsion layer is the outermost layer to limit the nucleation and reduction of the residual silver halide of that layer to the exclusion of the other layer. Ordinarily the combined nucleating and developing activity of the boron compound-hydroquinone derivative compositions is confined to an outer silver halide emulsion layer although an underlying emulsion layer will usually be nucleated by the borohydride component of the solution.

Our invention is primarily directed to the use of the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloriodide, -chlorobromiodide, -bromide and bromiodide developing-out emulsions. While the results in the following examples are obtained using gelatino-silver-bromiodide emulsions, excellent results can also be obtained using other photographic silver halide emulsions. These emulsions can be coated in the usual manner on any suitable support, e.g., glass, cellulose nitrate film, cellulose acetate film, polyester film, polyvinyl acetal resin film, paper, metal, etc.

The following examples will serve to illustrate our invention.

Example 1

A multilayer color film was provided including a cellulose ester film support having superimposed thereon in order red, green and blue light sensitive gelatin silver bromiodide emulsion layers, a yellow filter layer separating the blue and green sensitive emulsion layers. The film was exposed to a colored subject to record latent negative images in each emulsion layer. Thereafter the film was developed in a black-and-white silver halide developer solution such as the following:

55	Sodium sulfite (anhydrous)	g	80.0
	N-methyl-p-aminophenol sulfate	g	5.0
	Hydroquinone	g	2.0
	Sodium carbonate (monohydrate)	g	25.0
	Sodium bromide	g	2.0
70	Potassium iodide (0.1% solution)	cc	2.0
	Isopropylamine	g	6.0
	Water to make one liter.		

(pH was 10.3)

Following washing the red sensitive emulsion layer of the film was reversal exposed through the support using

red light and the film was then developed in a cyan color developer composition such as the following:

Sodium sulfite (anhydrous) -----g--	5.0
Color developer ¹ -----g--	0.55
Sodium carbonate (monohydrate) -----g--	15.00
Potassium bromide -----g--	0.25
Potassium iodide (0.1% solution) -----cc--	2.00
Color coupler ² -----g--	0.55
Sodium hydroxide -----g--	0.4
Water to make one liter.	

(pH was 10.0).

¹ 4-amino-3-methyl-N,N-diethylaniline hydrochloride.
² 2,4-dichloro-5-(p-toluenesulfonamido)-1-naphthol.

As a result a subtractively colored cyan dye image was formed in the red sensitive emulsion layer.

Following washing, the outer blue sensitive emulsion layer was incompletely exposed using blue light so as not to expose the underlying green sensitive emulsion layer; thereafter yellow color development was carried out in a color developer solution such as described above except containing as the coupler ω -benzoylacetanilide, thereby forming a subtractively colored yellow dye image in the layer.

The film was then treated for 30 seconds at 80° F. with the following bath to nucleate and develop the residual silver halide in the blue sensitive emulsion layer and to nucleate the silver halide in the green sensitive emulsion layer.

Water -----ml--	800
NaOH -----g--	3.0
KBH ₄ -----g--	0.10
Na ₂ SO ₃ -----g--	5.0
2,5-dihydroxy-n-nonanophenone -----g--	0.7
Water to make 1 liter.	

After washing the film was developed in a color developer composition such as described above except containing as the magenta color forming coupler 1-p-nitrophenyl-3-methyl-5-pyrazolone.

Subsequently the film was treated to remove the silver therefrom, by washing first for 5 minutes and then treating for 2 minutes in a silver bleach bath having the following composition:

Sodium ferricyanide -----G.	45
Sodium bromide -----	160
Sodium bromide -----	36
Water to make one liter.	

The film was then treated for 2 minutes in a fixing bath having the following composition:

Sodium hyposulfite -----G.	50
Sodium sulfite -----	180
Sodium sulfite -----	9.0
Water to make one liter.	

The film was then washed for 5 minutes and dried.

As a result cyan, magenta and yellow positive images were obtained in the red, green and blue sensitive emulsion layers, respectively, and it was apparent therefrom that the borohydride-hydroquinone derivative bath had been particularly effective to prevent the development of magenta dye in the blue sensitive emulsion layer and the development of yellow dye in the green sensitive emulsion layer.

Example 2

The process of Example 1 was carried out except using 0.5 gram of 2,5-dihydroxy-n-nonanophenone, and 0.2 gram of tertiarybutylamine borane instead of KBH₄ with similar results, the proper dye being developed in the blue and green sensitive emulsion layers.

Example 3

The process of Example 1 was carried out except using 0.5 gram of 2,5-dihydroxy-n-nonanophenone, and 0.2 gram of dimethylamine borane instead of KBH₄ with

similar results, the proper dye being developed in the blue and green sensitive emulsion layers.

Example 4

The process of Example 1 was carried out except using 0.5 gram of 2,5-dihydroxy-n-nonanophenone, and 0.2 gram of trimethylamine borane instead of KBH₄ with similar results, the proper dye being developed in the blue and green sensitive emulsion layers.

Example 5

The process of Example 1 was carried out except using 0.5 gram of 2,5-dihydroxy-n-nonanophenone, and 0.4 gram of pyridine borane instead of KBH₄ with similar results, the proper dye being developed in the blue and green sensitive emulsion layers.

In a similar manner other multilayer color films containing at least two differently sensitized emulsion layers, at least one emulsion layer being primarily blue sensitive and one or more other emulsion layers red or green light sensitive, can be color developed as described above using the borohydride-hydroquinone derivative bath prior to the last color development step. Thus, following reversal exposure and color development of the blue sensitive emulsion layer (or other outer emulsion layer) the bath is employed to nucleate and develop residual silver halide in the blue sensitive emulsion layer and to nucleate the other layer or layers of the same or different light sensitivity adjacent thereto. Thereafter, the remaining layer or layers are color developed and silver and any residual silver halide are removed as usual.

The first or black-and-white developer used in the process of our invention is generally a rapid developer of the MQ type, i.e., a combination of hydroquinone and Elon (p-N-methylaminophenol) developer, or a Phenidone (a 3-pyrazolidone) developer.

The color-forming developers useful in our invention have been previously described in the prior art, and our invention is not to be restricted to the use of any particular color-forming developer. Color-forming developers particularly useful in practicing the process of our invention comprise the aromatic primary amines containing an additional substituent (i.e., additional to the primary amino group) selected from an amino group (substituted or not) and a hydroxyl substituent. Such color developers comprise the phenylenediamines and substituted derivatives thereof containing at least one primary amino group, such as the color-forming developers disclosed in Weissberger U.S. Patent 2,548,574, dated April 10, 1951, Weissberger et al. U.S. Patent 2,566,271, dated August 28, 1951, etc. Aminophenols containing at least one primary amino group can also be used as color developers.

The usual addends can be incorporated in the color developers, such as strongly alkaline agents (e.g., sodium carbonate, potassium carbonate, sodium hydroxide, etc.), restraining agents, such as potassium bromide, stain preventives, such as alkali metal sulfites, etc. As indicated above, the color-forming compounds or couplers are also used in the color developers. The prior art has previously described in detail many water-soluble color couplers which can be used in the process of our invention. Typical of such couplers are the following:

Cyan couplers:

- (1) 5-benzenesulfonamino-1-naphthol
- (2) 2,4-dichloro-5-(p-toluenesulfamino)-1-naphthol
- (3) 2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
- (4) 5-(m-nitrobenzenesulfonamino)-1-naphthol
- (5) 2-acetylamino-5-methylphenol
- (6) 2- α -(p-tert. amylphenoxy)-n-butyrylamino-4-chloro-5-methylphenol
- (7) 2-(p'-tert. amylphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
- (8) 2-phenylacetylamino-4-chloro-5-methylphenol

- (9) 2-anilinoacetyl-amino-4-chloro-5-methylphenol
- (10) 2-{4'-[3''-(4'''-tert. amylphenoxy)-benzoyl-amino]benzoylamino}-4-chloro-5-methylphenol
- (11) 2-m-aminobenzoyl-4-chloro-5-methylphenol
- (12) 2-(4'-sec. amylbenzamino)-4-chloro-5-methylphenol

Magenta couplers:

- (13) 1-phenyl-3-acetyl-amino-5-pyrazolone
- (14) 1-phenyl-3-dichloroacetyl-amino-5-pyrazolone
- (15) 1-phenyl-3-(m-aminobenzoyl)-amino-5-pyrazolone hydrochloride
- (16) 1-phenyl-3-phenylcarbonylamino-5-pyrazolone
- (17) 1-phenyl-3-p-aminobenzoylamino-5-pyrazolone
- (18) 1-phenyl-3-palmityl-amino-5-pyrazolone
- (19) 1-phenyl-3-[p-(p'-sec. amylbenzoyl)amino-benzoylamino]-5-pyrazolone
- (20) 1-m-tolyl-3-(2,4-di-tert. butyl-m-tolyl-oxyacetyl-amino)-5-pyrazolone
- (21) 1-(m-tert. butylphenoxyphenyl)-3-(p-n-amyloxybenzoylamino)-5-pyrazolone
- (22) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-[m-(p-toluenesulfonylamino)benzoylamino]-5-pyrazolone
- (23) 3-(p-nitrophenoxyacetyl-amino)-1-(2',4',6'-trichlorophenyl)-5-pyrazolone

Yellow couplers:

- (24) p-(ω -benzoylacetamino)benzenesulfonamide
- (25) p-(ω -benzoylacetamino)benzenesulfonanilide
- (26) 4-(p-toluenesulfonamino)- ω -benzoylacetanilide
- (27) 1,4-di-[p-(benzoylacetamino)benzenesulfonamino]benzene
- (28) N-(p-benzoylacetaminophenyl)-4-[p-(benzoylacetamino)-benzenesulfonamido]-benzenesulfonamide
- (29) p-acetoacetaminobenzenesulfon- β -naphthalide
- (30) p-(4-ethoxybenzoylacetamino)benzenesulfonamide
- (31) p-(quinoline-8-sulfonamino)- ω -benzoylacetanilide
- (32) N,N'-di-(p-benzoylacetaminophenol)-naphthalene-1,5-disulfonamide
- (33) N-benzoylacetato-o-anisidine

Other water-soluble color-forming compounds or couplers can be employed in practicing the process of our invention.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

What we claim is:

1. In the reversal process of producing a color record in a photoexposed photographic element having on a support a plurality of silver halide emulsion layers sensitive to different regions of the visible spectrum, said reversal process including the steps of producing a negative silver image in at least one of said emulsion layers by development in a black-and-white photographic developer, followed by at least one reversal re-exposure of previously unexposed silver halide and developing in a photographic color developer in the presence of a color-forming coupler, the improvement comprising after said re-exposure and development in a color developer, the step of eliminating a last reversal re-exposure by imbibing in said photographic element an aqueous solution containing a boron compound nucleating agent selected from the class consisting of alkali metal borohydrides, borazines, amine boranes, hydrazine boranes, phosphine boranes, arsine boranes, and stibine boranes, and a 1,4-

dihydroxybenzene developing agent which contains a side chain containing at least 4 carbon atoms, said 1,4-dihydroxybenzene compound being rendered non-diffusible by said side chain and thereby being confined substantially to the outermost of said emulsion layers with respect to said support, said boron compound nucleating agent nucleating substantially all previously unexposed silver halide and said 1,4-dihydroxybenzene compound developing to metallic silver substantially only the previously unexposed silver halide in said outermost emulsion layer.

2. The process of claim 1 wherein the boron compound is an alkali metal borohydride.

3. The process of claim 1 wherein the boron compound is an amine borane.

4. A process of producing a photographic color reproduction which comprises exposing to a colored subject a photographic element containing at least two photographic silver halide emulsion layers sensitized to different regions of the spectrum, one of the emulsion layers being primarily sensitive to the blue region of the spectrum, developing negative silver images in the exposed element by means of a black-and-white silver halide developing solution, reversal exposing the blue sensitive emulsion layer and developing a colored image therein by treating the element with a photographic color developing solution in the presence of a coupler compound which couples with the oxidation products of the color developer to form a dye image, treating the element with an alkaline solution of an alkali metal borohydride and a hydroquinone derivative which contains a chain of at least 4 carbon atoms, until any residual undeveloped silver halide in the blue-sensitive emulsion layer has been nucleated and reduced to silver and the silver halide in the other emulsion layer has been nucleated, and developing a colored image in said other emulsion layer by treatment of the element with a photographic color developing solution in the presence of a coupler compound which couples with the oxidation products of the color developer to form a colored image.

5. A process of producing a photographic color reproduction which comprises exposing to a subject a photographic element including red, green, and blue light-sensitive silver halide emulsions superposed in order on a support, developing negative silver images in the exposed element by means of a black-and-white silver halide developing solution, reversal exposing and developing a cyan dye image in the red-sensitive emulsion layer by treating the element with a photographic color developing solution in the presence of a coupler compound which couples with the oxidation products of a color developer to form a cyan dye image, reversal exposing a substantial amount of the residual undeveloped silver halide in the outer blue-sensitive emulsion layer and developing a yellow dye image therein by treating the element with a photographic color developing solution in the presence of a coupler compound which couples with the oxidation products of the color developer to form a yellow dye image, treating the element with an alkaline solution of an alkali metal borohydride and a hydroquinone derivative which contains a chain of at least 4 carbon atoms, until any residual undeveloped silver halide in the blue-sensitive emulsion layer has been reduced to silver and the undeveloped silver halide of the green-sensitive emulsion layer has been nucleated, developing a magenta image in the green-sensitive emulsion layer by treatment of the element with a photographic color developing solution in the presence of a coupler compound which couples with the oxidation products of the color developer to form a magenta dye image.

6. The process of claim 4 wherein the hydroquinone derivative is a member of the class consisting of t-butylhydroquinone, n-octylhydroquinone, n-nonylhydroquinone and 2,5-dihydroxyacylophenones the acyl group of which contains from 8 to 10 carbon atoms.

11

7. The process of claim 5 wherein the hydroquinone derivative is a 2,5-dihydroxyacylophenone the acyl group of which contains from 8-10 carbon atoms.

8. The process of claim 4 wherein the hydroquinone derivative is t-butylhydroquinone.

9. The process of claim 4 wherein the hydroquinone is n-octylhydroquinone.

10. The process of claim 4 wherein the hydroquinone derivative is n-nonylhydroquinone.

11. The process of claim 4 wherein the hydroquinone derivative is 2,5-dihydroxy-n-octanophenone.

12. The process of claim 4 wherein the hydroquinone derivative is 2,5-dihydroxy-n-nonanophenone.

13. The process of claim 4 wherein the hydroquinone derivative is 2,5-dihydroxy-n-decanophenone.

14. The process of claim 4 wherein the reversal exposure of the blue-sensitive emulsion layer is such as to incompletely expose the silver halide thereof.

15. The process of claim 5 wherein the reversal exposure of the blue-sensitive emulsion layer is such that the silver halide of a green-sensitive emulsion layer is not exposed thereby.

16. An aqueous alkaline photographic solution adapted to nucleate and reduce silver halide, comprising a boron compound nucleating agent selected from the class consisting of alkali metal borohydrides, borazines, amine boranes, hydrazine boranes, phosphine boranes, arsine boranes and stibine boranes, an alkali-soluble hydroquinone derivative containing a carbon chain of at least 4 carbon atoms.

12

17. The solution of claim 16 wherein the boron compound is an alkali metal borohydride.

18. The solution of claim 16 wherein the boron compound is an amine borane.

5 19. The solution of claim 16 wherein the hydroquinone compound is a member of the class consisting of t-butylhydroquinone, n-octylhydroquinone, n-nonylhydroquinone and 2,5-dihydroxyacylophenones the acyl group of which contains from 8 to 10 carbon atoms.

10 20. The solution of claim 16 wherein the hydroquinone compound is a 2,5-dihydroxyacylophenone the acyl group of which contains from 8 to 10 carbon atoms.

15 21. A composition for photographic processing adapted to nucleate and reduce silver halide comprising a boron compound selected from the class consisting of alkali metal borohydrides, borazines, amine boranes, hydrazine boranes, phosphine boranes, arsine boranes and stibine boranes, and an alkali-soluble hydroquinone derivative containing a carbon chain of at least 4 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

2,865,747 12/1958 Mader 96-66
25 2,984,567 5/1961 Henn et al. 96-59

NORMAN G. TORCHIN, *Primary Examiner.*

J. T. BROWN, *Assistant Examiner.*

30