

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Colour Reversal Process

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America (Assignees of PHILIP ERWIN PERKINS and HERBERT LLEWELLYN REES) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a photographic colour reversal process.

Colour films of the reversal type carry at least 2, and usually 3, silver halide emulsion layers sensitive to different regions of the spectrum. In a colour film having 3 emulsion layers usually the outer emulsion layer is blue-sensitive, the next inner emulsion layer is green-sensitive, while the emulsion layer adjacent to the support is red-sensitive. Between the blue-sensitive and green-sensitive emulsion layers there may be a filter layer for absorbing any blue radiation transmitted through the blue-sensitive layer. The multi-layer film can also have other interlayers for special purposes. Such multilayer colour films have been previously described in the prior art, such as U.K. specification 507,841. After exposure to a light image 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 colour-forming developer composition containing a cyan colour-forming coupler and a p-phenylenediamine silver halide developing agent the oxidation product of which is reactive with the coupler to form a cyan dye image, the blue-sensitive emulsion layer is then reversal exposed and developed in a colour developer containing a yellow colour-forming

coupler to develop a yellow dye image in the layer, following which the middle, green-sensitive, emulsion layer is reversal exposed and developed with a colour developing solution containing a magenta colour-forming coupler, or the reversal exposure of the green-sensitive emulsion layer may be dispensed with and instead a fogging magenta colour developer can be used for forming the magenta image in the green-sensitive emulsion layer.

In processing reversal colour films in this manner it is difficult to prevent dye images of the wrong colour being developed in the emulsion layers. Thus, if the reversal exposure of the silver halide in the blue-sensitive emulsion layer has not been adequate, magenta dye can be developed in the layer which should contain only a yellow dye image when the green-sensitive layer is colour reversal developed. 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 exposure step before the yellow colour development step. Because of inadequate protection of the middle layer, by even a 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 colour development, they will be developed in the yellow colour developer giving yellow dye contamination in the middle

[Price 4s. 6d.]



layer. Thus, 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. On the other hand, 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 colour 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 colour developer a black-and-white auxiliary developer must be used to complete development of the top layer and this may also fog the middle layer.

According to the present invention there is provided a colour process wherein a photographic material which comprises a support and at least an outer silver halide emulsion layer and a next inner silver halide emulsion layer which is sensitive to a part of the region of the spectrum to which the outer layer is sensitive is exposed to a light image and developed by a black and white developer, thereby producing a negative silver image and a complementary silver halide image in each of the emulsion layers, the outer emulsion layer is subjected to a reversal re-exposure without rendering developable silver halide in the inner emulsion layer, the outer emulsion layer is colour developed by a colour developer in the presence of a colour forming coupler, the material is treated with an aqueous solution which contains a silver halide nucleating boron compound having at least one boron atom bonded to at least one hydrogen atom so as to nucleate residual silver halide in the outer emulsion layer and the silver halide image in the inner emulsion layer and at the same time or thereafter the material is treated with an alkaline aqueous solution which contains a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and having a side chain containing at least 4 C atoms substituted in the nucleus so as to reduce to silver only the nucleated silver halide in the outer emulsion layer.

By the process of the present invention there is produced a photographic material in which, after colour development of the inner emulsion layer, the emulsion layers are free from alien dyes. To render the dye images clearly visible the developed silver in the layers is removed, e.g. by bleaching and fixing. The emulsion layers are usually colour developed to reversal dye images which are subtractively coloured relative to the sensitivities of the emulsion layers.

In the photographic material which is pro-

cessed according to this invention there may be a filter layer between the outer and next inner emulsion layers which absorbs light to which the outer emulsion layer is sensitive. The outer emulsion layer is preferably blue sensitive and the next inner emulsion layer green sensitive. A filter layer between these layers will usually be yellow (blue-light absorbing).

The process of the present invention is useful for the processing of film of the reversal type, particularly 'Kodachrome' (registered trade mark) which contains three differentially sensitive emulsion layers the outer emulsion layer being blue sensitive, the next inner emulsion layer green sensitive and the emulsion layer nearest the support red sensitive. The film also comprises a yellow filter (blue light absorbing) between the outer and next inner emulsion layers. These layers are processed so as to form a cyan image in the red sensitive emulsion layer, a yellow dye image in the blue sensitive emulsion layer and a magenta dye image in the green sensitive emulsion layer.

Preferably in the process of the invention the aqueous solution of the boron compound and alkaline solution of the 1,4-dihydroxybenzene derivative are combined in a single nucleating and developing solution for the simultaneous treatment of the photographic material therewith. Such solutions are described and claimed in our divisional application No 56422/66 (Serial No 1089992).

When the combined nucleating and developing bath is used according to this invention for processing film of the reversal type, e.g. "Kodachrome" (registered trade mark), following colour development of the outer, blue sensitive, emulsion layer and prior to the last colour development step, any residual undeveloped silver halide in the blue sensitive emulsion layer is nucleated and reduced to silver without development of the silver in the adjacent inner, 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 colour developer containing a magenta colour forming coupler can be used. Accordingly, in the reversal exposure of the blue sensitive emulsion layer in the process of this invention 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 boron compound-hydroquinone derivative compositions can also 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.

The 1,4-dihydroxybenzene derivatives having a chain containing at least 4 C atoms substituted in the nucleus which are used to develop nucleated silver halide in the method of the invention are soluble in alkaline aqueous solution. The 1,4-dihydroxybenzene derivatives of high molecular weight should also contain solubilising groups such as sulpho and carboxyl groups to increase the solubility of the compound in alkaline solution. The carbon chain of at least 4 C atoms may include the carbon atoms of a cyclic radical for example, as present in the 8-carbon atom chain of the $-C_6H_4-C_2H_4-$ radical of compounds 10 and 11.

The hydroquinone derivatives (i.e. 1,4-dihydroxybenzene derivatives) which may be used in a combined nucleating and developing bath in the invention preferably contain 4 to 20° C atoms in the nuclear substituted chain. The 2,5-dihydroxyacylophenones containing 8 to 10 C atoms in the acyl groups, as in compounds 5, 6 and 7 below are very useful. Exemplary hydroquinone derivatives are:

1. t-butylhydroquinone
2. n-hexylhydroquinone
3. n-octylhydroquinone
4. n-nonylhydroquinone
5. 2,5-dihydroxy-n-octanophenone
6. 2,5-dihydroxy-n-nonanophenone
7. 2,5-dihydroxy-n-decanophenone
8. 2 - n - octylhydroquinone - 5-sulphonic acid, sodium salt
9. 2 - (sec - octadecyl) - 5 - (sulpho - t-butyl)hydroquinone, sodium salt, dihydrate
10. 2 - [4'-(3'',5'' - disulpho benzamido)] phenethylhydroquinone, disodium salt, dihydrate
11. 5 - [4'-(3'',5'' - disulphobenzamido)] phenethyl - 2 - methylhydroquinone, disodium salt.

These compounds are characterised by having good solubility in alkaline aqueous solution and a low rate of diffusion through photographic emulsion layers, such as gelatin silver halide emulsion layers whereby the reduction of the nucleated silver halide can be confined to the nucleated silver halide in the outermost emulsion layer such as the outer blue sensitive emulsion layer of a conventional multilayer colour film.

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 same time as 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, laurylhydro-

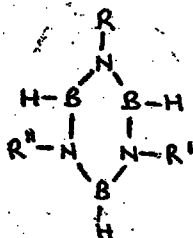
quinone, cyclohexylhydroquinone and 2,5-dicyclohexylhydroquinone are not useful in the process particularly because their solubilities in the alkaline solution are too low. It should be particularly noted that while the 2,5-dihydroxyacylohydroquinones such as 5, 6 and 7 above, e.g. 2,5-dihydroxynonaphenone are very useful, the compound 2,5-dihydroxydodecanophenone is not useful in the process of the invention.

It is believed that when these latter compounds 5, 6 and 7 are used in the nucleating and developing bath, in the presence of a borohydride compound they are reduced to the corresponding alcohols. Thus, the groups $-COC_6H_{17}$, $-COC_7H_{15}$ and $-COC_8H_{13}$ of these compounds are reduced to $-CH(OH)C_6H_{17}$, $-CH(OH)C_7H_{15}$ and $-CH(OH)C_8H_{13}$ 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 the use of compositions containing either form of the compounds in conjunction with the boron compounds.

The boron compound nucleating agents for silver halide are boron compounds containing at least one boron atom bonded to at least one hydrogen atom. Thus, the boron compounds include the boranes and borazenes. Examples of the boron compounds which may be used are the alkali metal borohydrides, e.g. potassium and sodium borohydrides (KBH_4 and $NaBH_4$) and the amine boranes such as aliphatic amine boranes, arylamine boranes and cyclic amine boranes. Thus the amine boranes include those of formula ZBH_3 in which Z represents ammonia, a mono- di- or tri-alkylamine, a mono- or di-hydroxylamine, 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 and tertiary-amylamine. The amine boranes also include those which contain a polyamine or a hydrazine in which each of the amine groups is bonded to a BH_3 group for example of formula $Z(BH_3)_2$ wherein Z is $NH_2CH_2CH_2NH_2$ or NH_2NH_2 . The above formula may also represent an arylamine in which for example Z is aniline or may represent a cyclic amine in which for example Z is 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 and 3-propylpyridine. In the above formula Z may also be a phosphine such as an alkylphosphine, for example methyl phosphine, dimethylphosphine, trimethylphosphine, ethylphosphine, diethylphosphine, triethylphosphine, propylphosphine, dipropylphosphine, tripropylphos-

di-hydroxyalkylamine

phine, primary-butylphosphine, and secondary-butylphosphine) an aryl phosphine, (for example, phenylphosphine), an arsine, such as an alkylarsine, (for example methylarsine, dimethylarsine, trimethylarsine, propylarsine, primary - butylarsine, secondary - butylarsine and amylarsine), an arylarsine, (for example, phenylarsine) or a stibine, such as an alkylstibine, (for example, methylstibine, dimethylstibine, trimethylstibine, ethylstibine, diethylstibine, triethylstibine, propylstibine, primary-butylstibine, secondary-butylstibine and tertiary-butylstibine) or an arylstibine, (for example, phenylstibine). The borazene nucleating agents may be represented by the formula:



wherein R, R' and R'' each represent an H atom, a halogen atom, (such as chlorine, bromine, fluorine or iodine) an alkyl group, (preferably lower alkyl containing from 1 to 4 C atoms, such as methyl, ethyl, propyl and butyl) or an alkoxy group (preferably lower alkoxy containing from 1 to 4 C atoms, such as methoxy, ethoxy, propoxy and butoxy).

Included among the boron compound nucleating agents which may be used in the invention are the following:

- 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
- Borazenes
- Borazene
- N,N',N''-trimethyl borazene
- N,N',N''-trimethoxy borazene

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 Pittsburg, Pennsylvania.

The phosphine boranes, the arsine boranes and stibine boranes are described in U.S.P. 2,999,864.

The boranes are synthesised by condensation of diborane with the appropriate nitrogen compound. For example, borazene is made by condensing diborane with ammonia. N,N',N''-trialkylborazene is produced by condensing diborane with the corresponding N-alkylamine. An N,N'-dialkyl borazene is produced by condensing diborane with a mixture of ammonia and the appropriate N-alkylamine.

The alkaline aqueous solutions containing the effective hydroquinone derivatives and boron compounds should be strongly alkaline having a pH of at least 10. From 0.05g to 10g or more of the boron compound may be used per litre, preferably from 0.1g to 0.5g per litre, and from 0.05 to 5g or more of the hydroquinone derivative per litre of solution preferably from 0.5g to 0.7g per litre. 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 the green sensitive or other inner emulsion layer during treatment of the blue sensitive or other outer emulsion layer with the alkaline solution of boron compound and hydroquinone derivative. The time of treatment of the films with the alkaline solutions can vary from 15 to 120 secs 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 solution 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 materials to which this invention may be applied preferably contain gelatin silver halide emulsion layers.

The silver halide in the emulsion layers present in the photographic materials used in this invention may be silver chloride, silver chlorobromide, silver chloroiodide, silver chlorobromiodide, silver bromide or silver bromiodide. The emulsions are developing-out emulsions. While the results in the

following Examples are obtained using gelatin silver bromide emulsions, excellent results can also be obtained using other photographic silver halide emulsions. These emulsions can be coated in the usual manner on any support, e.g. glass, cellulose nitrate film, cellulose acetate film, polyester film, polyvinyl acetal resin film, paper or metal.

The following are examples of the processes of the invention:

EXAMPLE 1

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

	grams
sodium sulphite (anhydrous)	80
N - methyl - p - aminophenol sulphate	5
hydroquinone	2
sodium carbonate (monohydrate)	25
sodium bromide	2
potassium iodide (0.1% solution)	2 c.c.
isopropylamine	6
water to make (pH was 10.3)	1 litre

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 colour developer composition of the following composition:

	grams
sodium sulphite (anhydrous)	5
colour developer*	0.55
sodium carbonate (monohydrate)	15
potassium bromide	0.25
potassium iodide (0.1% solution)	2 c.c.
colour coupler**	0.55
sodium hydroxide	0.4
water to make (pH was 10.0)	1 litre

*4 - amino - 3 - methyl - N,N - diethylaniline hydrochloride

**2,4 - dichloro - 5 - (p - toluenesulphonamido)-1-naphthol

As a result a subtractively coloured 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 colour development was carried out in a colour developer solution such as described above except that it contained as the coupler ω -benzoylacetanilide which formed a subtractively coloured yellow dye image in the layer.

The film was then treated for 30 secs at 80° F with the following bath to nucleate and develop the residual silver halide in the blue sensitive emulsion layer and to nucleate but not develop the silver halide in the green sensitive emulsion layer.

	grams
water	800 ml
NaOH	3
KBH ₄	0.1
Na ₂ SO ₃	5
2,5-dihydroxy-n-nonanophenone	0.7
water to make	1 litre

After washing, the film was developed in a colour developer composition such as described above except that instead of the cyan colour coupler the magenta colour forming coupler 1-p-nitrophenyl-3-methyl-5-pyrazolidone was used.

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

	grams
sodium ferricyanide	160
sodium bromide	36
water to make	1 litre

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

	grams
sodium hyposulphite	180
sodium sulphite	9
water to make	1 litre

The film was then washed for 5 mins 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 0.5g of 2,5-dihydroxy-n-nanophenone and 0.2g of tertiary-butylamine borane instead of KBH_4 with similar results, the correct dye being developed in the blue and green sensitive emulsion layers.

EXAMPLE 3

The process of Example 1 was carried out except using 0.5g of 2,5-dihydroxy-n-nanophenone and 0.2g of dimethylamine borane instead of KBH_4 with similar results, the correct dye being developed in the blue and green sensitive layers.

EXAMPLE 4

The process of Example 1 was carried out except using 0.5g of 2,5-dihydroxy-n-nanophenone and 0.2g of trimethylamine borane instead of KBH_4 with similar results, the correct dye being developed in the blue and green sensitive emulsion layers.

EXAMPLE 5

The process of Example 1 was carried out except using 0.5g of 2,5-dihydroxy-n-nanophenone and 0.4g of pyridine borane instead of KBH_4 with similar results, the correct dye being developed in the blue and green sensitive emulsion layers.

In a similar manner other multilayer colour films containing at least 2 differently sensitised emulsion layers, at least 1 emulsion layer being primarily blue sensitive and one or more other emulsion layers red or green light sensitive, can be colour developed as described above using the borohydride and hydroquinone derivative-containing bath prior to the last colour development step. Thus, following reversal exposure and colour 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 adjacent thereto having a light-sensitivity to regions overlapping those of the outer layer. Thereafter, the remaining layer or layers are colour developed and silver and any residual silver halide is 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 mixture of hydroquinone and Elon (p-N-methylaminophenol) developer, or a Phenidone (a 3-pyrazolidone) developer. "Elon" and "Phenidone" are registered trade marks.

The colour forming developers useful in our invention have been previously described in the prior art and our invention is not restricted to the use of any particular colour forming developer. Colour forming developers particularly useful in practicing

the process of this 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 colour developers comprise the phenylene-diamines and substituted derivatives thereof containing at least 1 primary amino group, such as the colour forming developers disclosed in U.K. patents 651,749 and 653,284. Aminophenols containing at least 1 primary amino group can also be used as colour developers.

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

Cyan Couplers

1. 5-benzenesulphonamido-1-naphthol
2. 2,4 - dichloro - 5 - (p - toluenesulphamido) - 1 - naphthol 90
3. 2,4 - dichloro - 5 - (4' - bromodiphenyl - 4 - sulphonamido) - 1 - naphthol
4. 5 - (m - nitrobenzenesulphonamido)-1-naphthol 95
5. 2-acetyl-amino-5-methylphenol
6. 2 - a - (p - tert.amylphenoxy) - n-butylamino - 4 - chloro - 5 - methylphenol 100
7. 2 - (p' tert.amylphenoxy - p - benzoyl) amino-4-chloro-5-methylphenol
8. 2 - phenylacetyl-amino - 4 - chloro - 5 - methylphenol
9. 2 - anilinoacetyl-amino - 4 - chloro - 5 - methylphenol 105
10. 2 - {4' - [3'' - (4''' - tert.amylphenoxy) - benzoylamino]benzoylamino} - 4 - chloro - 5 - methylphenol
11. 2 - m - aminobenzoyl - 4 - chloro - 5 - methylphenol 110
12. 2 - (4' - sec.amylbenzamide) - 4 - chloro - 5 - methylphenol

Magenta Couplers

13. 1 - phenyl - 3 - acetyl-amino - 5 - pyrazolone 115
14. 1 - phenyl - 3 - dichloroacetyl-amino-5-pyrazolone
15. 1 - phenyl - 3 - (m - aminobenzoyl)-amino - 5 - pyrazolone hydrochloride 120
16. 1 - phenyl - 3 - phenylcarbamyl-amino-5-pyrazolone
17. 1 - phenyl - 3 - p - aminobenzoyl-amino-5-pyrazolone



18. 1 - phenyl - 3 - palmitylamino - 5 - pyrazolone
19. 1 - phenyl - 3 - [p-(p' - sec.amyl-benzoyl)aminobenzoylamino] - 5 - pyrazolone
20. 1 - m - tolyl - 3 - (2,4 - di - tert.butyl-m - tolyloxyacetyl-amino) - 5 - pyrazolone
21. 1 - (n - tert.butylphenoxyphenyl) - 3 - (p - n - amyloxybenzoylamino) - 5 - pyrazolone
22. 1 - [p - (p' - tert.butylphenoxy)phenyl] - 3 - [m - (p - toluenesulphonylamino) benzoylamino] - 5 - pyrazolone
23. 3 - (p - nitrophenoxyacetyl-amino) - 1 - (2',4',6' - trichlorophenyl) - 5 - pyrazolone

Yellow Couplers

24. p - (ω - benzoylacetamido)benzenesulphonamide
25. p - (ω - benzoylacetamido)benzenesulphonanilide
26. 4 - (p - toluenesulphonamido) - ω - benzoylacetanilide
27. 1,4 - di - [(benzoylacetamido)benzenesulphonamido]benzene
28. N - (p - benzoylacetamidophenyl) - 4 - [p - (benzoylacetamido) - benzenesulphonamido]benzenesulphonamide
29. p - acetoacetamidobenzenesulphon - β - naphthalide
30. p - (4 - ethoxybenzoylacetamido)benzenesulphonamide
31. p - (quinoline - 8 - sulphonamido) - ω - benzoylacetanilide
32. N,N' - di - (p - benzoylacetamidophenyl)naphthalene - 1,5 - disulphonamide
33. N-benzoylacetato-o-anisidine

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

Methods of producing a reversal colour image in which an aqueous alkali metal borohydride solution is employed to render developable all or part of the residual silver halide in an exposed and developed silver halide emulsion layer and in which the layer is subsequently colour developed are claimed in the claims of U.K. specification 904,462 (Kodak Limited).

A process of rendering developable a photographic layer having an image-wise distribution of silver halide which comprises subjecting said layer to treatment with an aqueous solution of a boron compound which has at least one and not more than three hydrogen to boron bonds or which contains two or more amine groups each bonded to a BH_3 is claimed in claim 1 of U.K. Specification 1,056,454 (Eastman Kodak Company).

photographic material which comprises a support and at least an outer silver halide emulsion layer and a next inner silver halide emulsion layer which is sensitive to a part of the region of the spectrum to which the outer layer is sensitive is exposed to a light image and developed by a black and white developer thereby producing a negative silver image and a complementary silver halide image in each of the emulsion layers, the outer emulsion layer is subjected to a reversal re-exposure without rendering developable silver halide in the inner emulsion layer, the outer emulsion layer is colour developed by a colour developer in the presence of a colour forming coupler, the material is treated with an aqueous solution which contains a silver halide nucleating boron compound having at least one boron atom bonded to at least one hydrogen atom so as to nucleate residual silver halide in the outer emulsion layer and the silver halide image in the inner emulsion layer and at the same time or thereafter the material is treated with an alkaline aqueous solution which contains a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and having a side chain containing at least 4 C atoms substituted in the nucleus so as to reduce to silver only the nucleated silver halide in the outer emulsion layer.

2. A colour reversal process according to claim 1 in which there is a filter layer between said outer and next inner silver halide emulsion layer which absorbs light to which said outer emulsion layer is sensitive.

3. A method according to claim 1 or 2 in which said next inner silver halide emulsion layer is sensitive to the green region of the spectrum and said outer silver halide emulsion layer is sensitive to the blue region of the spectrum.

4. A method according to claim 2 and 3 in which there is a yellow filter (i.e. which absorbs blue light) between the blue sensitive emulsion layer and the green sensitive emulsion layer.

5. A method according to any of claims 1 to 4 wherein the reversally re-exposed outer emulsion layer and the nucleated inner emulsion layer are each colour developed to a colour which is subtractively related to their sensitivities.

6. A colour reversal process according to claim 3 or 4 wherein the photographic material also comprises a red-sensitive silver halide emulsion layer between the green-sensitive emulsion layer and the support and, following the production of a negative silver image and a complementary silver halide image in each of the emulsion layers and before subjecting the outer emulsion layer to said reversal re-exposure, the red-sensitive emulsion layer is reversal colour developed to form a cyan dye image therein and wherein

WHAT WE CLAIM IS:—

1. A colour reversal process wherein a



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* C L M S *

- 5 18. 1 - phenyl - 3 - palmitylamino - 5 - pyrazolone
- 10 19. 1 - phenyl - 3 - [p-(p' - sec.amylbenzoyl)aminobenzoylamino] - 5 - pyrazolone
- 20 20. 1 - m - tolyl - 3 - (2,4 - di - tert.butyl - m - tolyloxyacetyl amino) - 5 - pyrazolone
21. 1 - (n - tert.butylphenoxyphenyl) - 3 - (p - n - amyloxybenzoylamino) - 5 - pyrazolone
22. 1 - [p - (p' - tert.butylphenoxy)phenyl] - 3 - [m - (p - toluenesulphonylamino)benzoylamino] - 5 - pyrazolone
- 15 23. 3 - (p - nitrophenoxyacetyl amino) - 1 - 2',4',6' - trichlorophenyl - 5 - pyrazolone

Yellow Couplers

- 20 24. p - (ω - benzoylacetamido)benzenesulphonamide
25. p - (ω - benzoylacetamido)benzenesulphonanilide
- 25 26. 4 - (p - toluenesulphonamido) - ω - benzoylacetanilide
27. 1,4 - di - [(benzoylacetamido)benzenesulphonamido]benzene
28. N - (p - benzoylacetamidophenyl) - 4 - [p - (benzoylacetamido) - benzenesulphonamido]benzenesulphonamide
- 30 29. p - acetoacetamidobenzenesulphon - β - naphthalide
30. p - (4 - ethoxybenzoylacetamido)benzenesulphonamide
- 35 31. p - (quinoline - 8 - sulphonamido) - ω - benzoylacetanilide
32. N,N' - di - (p - benzoylacetamidophenyl)naphthalene - 1,5 - disulphonamide
33. N-benzoylacetato-o-anisidine

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

45 Methods of producing a reversal colour image in which an aqueous alkali metal borohydride solution is employed to render developable all or part of the residual silver halide in an exposed and developed silver halide emulsion layer and in which the layer is subsequently colour developed are claimed in the claims of U.K. specification 904,462 (Kodak Limited).

50 A process of rendering developable a photographic layer having an image-wise distribution of silver halide which comprises subjecting said layer to treatment with an aqueous solution of a boron compound which has at least one and not more than three hydrogen to boron bonds or which contains two or more amine groups each bonded to a BH₃ is claimed in claim 1 of U.K. Specification 1,056,454 (Eastman Kodak Company).

photographic material which comprises a support and at least an outer silver halide emulsion layer and a next inner silver halide emulsion layer which is sensitive to a part of the region of the spectrum to which the outer layer is sensitive is exposed to a light image and developed by a black and white developer thereby producing a negative silver image and a complementary silver halide image in each of the emulsion layers, the outer emulsion layer is subjected to a reversal re-exposure without rendering developable silver halide in the inner emulsion layer, the outer emulsion layer is colour developed by a colour developer in the presence of a colour forming coupler, the material is treated with an aqueous solution which contains a silver halide nucleating boron compound having at least one boron atom bonded to at least one hydrogen atom so as to nucleate residual silver halide in the outer emulsion layer and the silver halide image in the inner emulsion layer and at the same time or thereafter the material is treated with an alkaline aqueous solution which contains a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and having a side chain containing at least 4 C atoms substituted in the nucleus so as to reduce to silver only the nucleated silver halide in the outer emulsion layer.

2. A colour reversal process according to claim 1 in which there is a filter layer between said outer and next inner silver halide emulsion layer which absorbs light to which said outer emulsion layer is sensitive.

3. A method according to claim 1 or 2 in which said next inner silver halide emulsion layer is sensitive to the green region of the spectrum and said outer silver halide emulsion layer is sensitive to the blue region of the spectrum.

4. A method according to claim 2 and 3 in which there is a yellow filter (i.e. which absorbs blue light) between the blue sensitive emulsion layer and the green sensitive emulsion layer.

5. A method according to any of claims 1 to 4 wherein the reversally re-exposed outer emulsion layer and the nucleated inner emulsion layer are each colour developed to a colour which is subtractively related to their sensitivities.

6. A colour reversal process according to claim 3 or 4 wherein the photographic material also comprises a red-sensitive silver halide emulsion layer between the green-sensitive emulsion layer and the support and, following the production of a negative silver image and a complementary silver halide image in each of the emulsion layers and before subjecting the outer emulsion layer to said reversal re-exposure, the red-sensitive emulsion layer is reversal colour developed to form a cyan dye image therein and wherein

WHAT WE CLAIM IS:—

1. A colour reversal process wherein a

the outer emulsion layer and the next inner emulsion layer are reversal colour developed to form therein respectively a yellow dye image and a magenta dye image and the developed silver is removed.

7. A process according to any of the preceding claims said side chain being t-butyl, n-octyl, or n-nonyl.

8. A process according to any of claims 1 to 6, said side chain being an alkanoyl group containing from 8 to 10 C atoms or the corresponding α -hydroxyalkyl group containing from 8 to 10 C atoms.

9. A process according to claim 8, said side chain being $n-C_7H_{15}CO-$, $n-C_8H_{17}CO-$ or $n-C_9H_{19}CO-$ or $n-C_7H_{15}CH(OH)-$, $n-C_8H_{17}CH(OH)-$ or $n-C_9H_{19}CH(OH)-$.

10. A method according to any of the preceding claims in which the boron compound is an alkali metal borohydride, an aliphatic amine borane, or a cyclicamine borane.

11. A method according to claim 10 in which the boron compound is KBH_4 , t-butylamine borane, dimethylamine borane, trimethylamine borane or pyridine borane.

12. A method according to any of the preceding claims in which the solution of the

boron compound contains from 0.1g to 0.5g of the compound per litre.

13. A method according to any of the preceding claims in which the alkaline solution containing the 1,4-dihydroxybenzene derivative contains from 0.05 to 5g of the derivative per litre.

14. A method according to claim 13 in which said alkaline solution contains from 0.5 to 0.7g of the 1,4-dihydroxybenzene derivative per litre.

15. A method according to any of claims 1 to 5 in which the material is treated with the alkaline solution containing the 1,4-dihydroxybenzene derivative and the aqueous solution containing the boron compound simultaneously, the two solutions being employed as a single solution having a composition substantially that of the composition containing 2,5-dihydroxynonanophenone defined in Example 1, 2, 3, 4 or 5.

16. A colour reversal process substantially as described in any of Examples 1 to 5 herein.

17. A photographic material comprising dye images which have been formed by a process according to any of claims 1 to 16.

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