

1089,992

PATENT SPECIFICATION

NO DRAWINGS

1089,992



Date of Application and filing Complete Specification: Nov. 16, 1964.

No. 56422/66.

Application made in United State of America (No. 323586) on Nov. 14, 1963.

(Divided out of No. 1089991).

Complete Specification Published: Nov. 8, 1967.

© Crown Copyright 1967.

Index at acceptance:—G2 CC10D

Int. Cl.:—G 03 c 5/50

COMPLETE SPECIFICATION

Photographic Nucleating and Developing Solution

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 processing solution containing a silver halide nucleating agent and a silver halide developing agent.

In our parent application 46674/64 (Serial No. 1089991) there is described and claimed a colour reversal 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.

The present invention relates particularly to a solution which can be used in the above process for treating the photographic material with the alkaline aqueous solution containing the 1,4 - dihydroxybenzene at the same time as it is treated with the aqueous solution containing the silver halide-nucleating boron compound.

According to the present invention there is provided an alkaline aqueous solution containing a silver halide-nucleating boron compound containing at least one boron atom bonded to at least one hydrogen atom and a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and having a side chain containing a chain of at least 4 C atoms substituted in the nucleus, the alkalinity of the solution and the concentrations of the boron compound and 1,4-dihydroxybenzene being such that, on contacting the solution with silver halide in a silver halide emulsion layer the silver halide is nucleated by the boron compound and the nucleated silver halide reduced to silver by the 1,4-dihydroxybenzene.

The alkaline solutions containing the effective hydroquinone derivatives and boron compound are preferably strongly alkaline having a pH of at least 10.

The solution may be made alkaline by a strong organic or inorganic alkali such as alkali metal hydroxide and quaternary ammonium hydroxide. Other addenda commonly

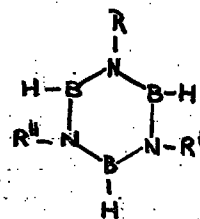
[Price 4s. 6d.]

used in photographic developer compositions may be added.

From 0.05 to 10g or more of the boron compounds may be used and from 0.05 to 5g or more of the hydroquinone derivative per litre 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 a green sensitive (inner) emulsion layer during treatment of a blue sensitive (outer) emulsion layer with the alkaline solutions of boron compounds and hydroquinone derivatives. The preferred concentration of the boron compound in the solution is from 0.1 to 0.5 grams per litre and the preferred concentration of the 1,4 - dihydroxybenzene is from 0.5 to 0.7 grams per litre.

The boron compound nucleating agents for silver halide used in the solutions of this invention are boron compounds containing at least one boron atom bonded to at least one hydrogen atom. Thus, the boron compounds include the borohydrides, 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-hydroxyalkylamine, 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 $\text{Z}(\text{BH}_3)_2$ wherein Z is $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or NH_2NH_2 . The above formula ZBH_3 may also represent an arylamine borane in which for example Z is aniline or may represent a heterocyclic 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 and 3-propylpyridine. In the above formula ZBH_3 Z may also be a phosphine such as an alkyl phosphine, for example methyl phosphine, dimethylphosphine, trimethylphosphine, ethylphosphine, diethylphosphine, triethylphosphine, propylphosphine, dipropylphosphine, tripropylphosphine, primary-butylphosphine and secondary-butylphosphine, or an aryl phosphine, for example phenyl-

phosphine, or may be an arsine such as an alkylarsine, for example methylarsine, dimethylarsine, trimethylarsine, propylarsine, primary-butylarsine, secondary-butylarsine and amylarsine, or an arylarsine, for example, phenylarsine, or may be 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 of the formula:



wherein R, R' and R'' each represent an H atom, a halogen atom, such as chlorine, bromine, fluorine, iodine, an alkyl group, preferably lower alkyl containing from 1 to 4 C atoms, such as methyl, ethyl, propyl and butyl, 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 silver halide 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

Dimethylphosphine

105

110



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) describes 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 U.S.P. 2,999,854.

The borazenes 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. Borazenes are sometimes referred to as borazoles eg. in *Z anorg. allg. Chem.* 256 177 [1948].

The solution provided by the present invention is capable of nucleating unexposed silver halide in the photographic material and of developing the nucleated silver halide. The presence of the side chain having at least 4 C atoms in the 1,4-dihydroxybenzene derivative causes the derivative to diffuse slowly in photographic silver halide emulsion layers, particularly in gelatin-silver halide emulsion layers, whereby the development of the nucleated silver halide can be confined to the outer layer of the colour photographic material which is colour reversal processed according to the parent invention. Thus, n-propyl hydroquinone is not present in the solution of the invention because it would tend to cause development of the inner emulsion layer to take place at the same time as development of the residual silver halide in the outer emulsion layer. Also, the hydroquinone derivatives 2,5-di-t-butylhydroquinone, n-decylhydroquinone, laurylhydroquinone, cyclohexylhydroquinone and 2,5-dicyclohexylhydroquinone are not useful in the solution particularly because of low solubility in the alkaline solution.

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

The hydroquinone derivatives useful in a combined developer and reversal bath of the invention are those which are soluble in alkali-

line solution and contain a chain of at least 4 C atoms substituted in the benzene nucleus. Included among the hydroquinone derivatives which may be employed in this invention are the alkali-soluble alkyl hydroquinones, the alkyl group of which contains at least 4 C atoms, preferably 4 to 20 C atoms. The 2,5-dihydroxyacylophenones containing 8 to 10 C atoms in the alkanoyl 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 - sulphonie acid sodium salt
9. 2 - (sec - octadecyl) - 5 - (sulpho - t-butyl)hydroquinone, sodium salt
10. 2 - [4 - (3,5 - disulphobenzamido)] - phenylethylhydroquinone, disodium salt, dihydrate
11. 5 - [4 - (3,5 - disulphobenzamido)] - phenethyl - 2 - methyl - hydroquinone, disodium salt

These compounds are characterised by having good solubility in alkaline aqueous solution and possess the desired low rate 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 is believed that in a solution of the invention which has been prepared using a phenone of formula No. 5, 6 or 7 and a borohydride, the phenone may be reduced to the corresponding alcohol. Thus, it is believed that the groups $\text{--COC}_6\text{H}_5$, $\text{--COC}_6\text{H}_4$ and $\text{--COC}_6\text{H}_3$ may be reduced to $\text{--CH(OH)C}_6\text{H}_5$, $\text{--CH(OH)C}_6\text{H}_4$ and $\text{--CH(OH)C}_6\text{H}_3$ groups respectively.

The following are examples of the invention:

EXAMPLE 1

	grams	
water	800 ml	
NaOH	3	
KBH ₄	0.1	120
Na ₂ SO ₃	5	
2,5 - dihydroxy - n - nonanophenone	0.7	
water to make	1 litre	

EXAMPLES 2-5

The aqueous solutions of these Examples

were made up as in Example 1 but using the following pairs of 1,4 - dihydroxybenzene derivative and boron compound in place of the 1,4-dihydroxybenzene derivative and boron compound used in Example 1.

- a. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of tertiary butylamine borane
- b. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of dimethylamine borane
- 10 c. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of trimethylamine borane
- d. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.4g of pyridine borane.

WHAT WE CLAIM IS:—

- 15 1. An alkaline aqueous solution containing a silver halide-nucleating boron compound containing at least one boron atom bonded to at least one hydrogen atom and a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and
- 20 having a side chain containing a chain of at least 4 C atoms substituted in the nucleus, the alkalinity of the solution and the concentrations of the boron compound and 1,4-dihydroxybenzene being such that, on
- 25 contacting the solution with silver halide in a silver halide emulsion layer the silver halide is nucleated by the boron compound and

the nucleated silver halide reduced to silver by the 1,4-dihydroxybenzene.

2. A solution according to claim 1, said side chain being a straight chain alkyl group containing from 4 to 9 C atoms.

3. A solution according to claim 1, said side chain being a straight chain alkanoyl group containing from 8 to 10 C atoms.

4. A solution according to claim 1, said side chain being a straight chain α -hydroxy-alkyl group containing from 8 to 10 C atoms.

5. A solution according to any of the preceding claims, the boron compound being an alkali-metal borohydride.

6. A solution according to any of claims 1 to 4, the boron compound being an amine borane.

7. A solution according to claim 6, the boron compound being a mono(tertiaryalkyl)-amineborane.

8. A solution according to claim 6, the boron compound being a dialkylamine or a trialkylamineborane.

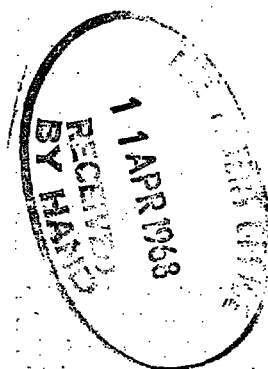
9. A solution according to claim 6, the boron compound being a heterocyclic amine borane.

10. A solution substantially as described in any of the Examples herein.

L. A. TRANGMAR, Bsc., C.P.A.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1967.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.



Kodak



were made up as in Example 1 but using the following pairs of 1,4 - dihydroxybenzene derivative and boron compound in place of the 1,4-dihydroxybenzene derivative and boron compound used in Example 1.

- 5
- a. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of tertiary butylamine borane
 - b. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of dimethylamine borane
 - 10 c. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.2g of trimethylamine borane
 - d. 0.5g of 2,5-dihydroxy-n-nonanophenone and 0.4g of pyridine borane.

WHAT WE CLAIM IS:—

- 15 1. An alkaline aqueous solution containing a silver halide-nucleating boron compound containing at least one boron atom bonded to at least one hydrogen atom and a silver halide developing agent which is a 1,4-dihydroxybenzene soluble in the solution and having a side chain containing a chain of at least 4 C atoms substituted in the nucleus, the alkalinity of the solution and the concentrations of the boron compound and 1,4-dihydroxybenzene being such that, on contacting the solution with silver halide in a silver halide emulsion layer the silver halide is nucleated by the boron compound and

the nucleated silver halide reduced to silver by the 1,4-dihydroxybenzene.

2. A solution according to claim 1, said side chain being a straight chain alkyl group containing from 4 to 9 C atoms.

3. A solution according to claim 1, said side chain being a straight chain alkanoyl group containing from 8 to 10 C atoms.

4. A solution according to claim 1, said side chain being a straight chain α -hydroxy-alkyl group containing from 8 to 10 C atoms.

5. A solution according to any of the preceding claims, the boron compound being an alkali-metal borohydride.

6. A solution according to any of claims 1 to 4, the boron compound being an amine borane.

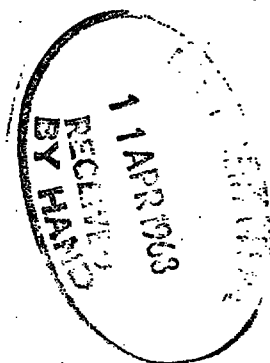
7. A solution according to claim 6, the boron compound being a mono(tertiaryalkyl)-amineborane.

8. A solution according to claim 6, the boron compound being a dialkylamine or a trialkylamineborane.

9. A solution according to claim 6, the boron compound being a heterocyclic amine borane.

10. A solution substantially as described in any of the Examples herein.

L. A. TRANGMAR, Bsc., C.P.A.



Kodak