

UNITED STATES PATENT OFFICE

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COLOR FORMING DEVELOPER AND PROCESS OF COLOR DEVELOPMENT

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This invention relates to photographic color development and to processes of color development for use in connection with color photography.

It is known that colored photographic images may be formed by using a developer which forms a colored and insoluble oxidation product during development, the colored product thus formed coloring the gelatine adjacent to the silver grains of the silver image. It is also known that a colored image may be formed by adding to certain developer solutions a compound which couples during development with the oxidation product of the developing agent and forms a coloring substance which is deposited adjacent to the developed silver grains.

Numerous substances have hitherto been employed or proposed to be employed as color couplers among which may be mentioned phenols, naphthols, cresols, nitrophenylacetone nitriles, aceto-acetic esters. It has not, however, always been possible to select from among those hitherto available one with which the oxidation product of the development agent gives the desired shade with regard to the colors which are already formed or which are bound to be formed in the other layers. A further limitation in the selection is due to the desirability of using such color couplers which give dyes insoluble in water and resist the effects of the employed photographic baths.

The present invention is based on the discovery of a new group of color couplers which in general satisfy the above requirements, and which are hydroxy-derivatives of diphenylmethane or phenyl-naphthyl-methane, in which both of the aromatic nuclei include at least one hydroxyl group. Such bodies have the following general formula:



where

X=Phenyl residue with one hydroxyl group in the ortho or para position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms (Cl or Br).

X'=Phenyl or naphthyl residue with one hydroxyl group in the ortho or para position with regard to CH₂, the remaining H-atoms of the phenyl or naphthyl residue can be substituted or not by halogens, alkyl-, aryl-, or aralkyl-groups, alkoxy, amino, or nitro-groups and in the case of a phenyl residue or the ring of a naphthyl-residue, which ring contains already an OH-group in the para-position to the CH₂ group, one or more of the remaining H-atoms may be substituted by the corresponding number of OH groups.

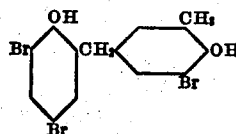
These color couplers form in general blue or blue-green colors on coupling with the oxidation product of aromatic amino developing agents during the development of the latent image.

The present invention consists in new or improved color forming developers comprising in addition to an aromatic amino-developing agent a color coupler as above defined. The present invention also includes a new or improved process or method of color development which comprises developing a latent photographic image by means of an aromatic amino-developer, in the presence of a color coupler as above defined, the silver image which is formed during development being eliminated so that a clear and transparent color image remains.

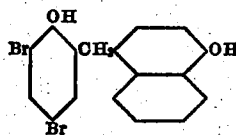
The present invention further includes photographic elements having at least one layer containing a clear transparent image composed essentially of the product resulting from the coupling in situ during development of a color coupler as above defined with the oxidation product of an aromatic amino developing agent.

Typical examples of suitable couplers within the scope of the invention are:

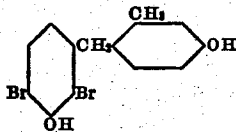
- (1) 4-(2'-hydroxy-3',5'-dibromobenzyl)-6-bromo-2-methyl-phenol:



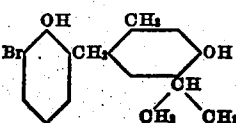
- (2) 4-(2'-hydroxy-3',5'-dibromobenzyl)-α-naphthol:



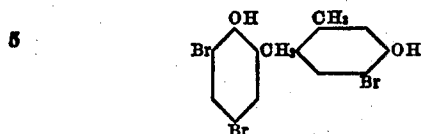
- (3) 4-(4'-hydroxy-3',5'-dibromobenzyl)-meta-cresol:



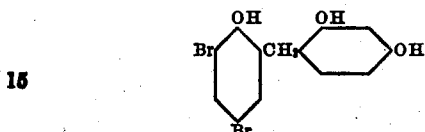
- (4) 4-(2'-hydroxy-3',5'-dibromobenzyl)-3-methyl-6-isopropyl phenol:



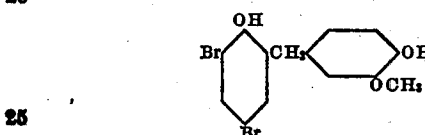
- (5) 4 - (2'hydroxy - 3',5'-dibromobenzyl) - 3-methyl-6-bromophenol:



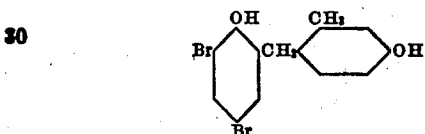
- 10 (6) 4 - (2'hydroxy - 3',5'- dibromobenzyl) - 1,3 dihydroxy benzene:



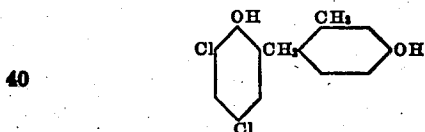
- 20 (7) 4-(2'hydroxy-3',5'-dibromobenzyl)-2 methoxy-phenol:



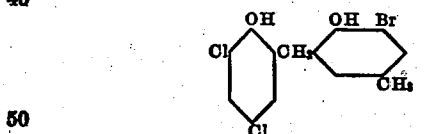
- 30 (8) 4-(2'hydroxy-3',5'-dibromobenzyl)-3 methyl phenol:



- 40 (9) 4-(2'hydroxy-3',5'-dichlorobenzyl)-3 methyl phenol:



- 50 (10) 2 - (2'hydroxy - 3',5' - dichlorobenzyl) -4-methyl-6-bromophenol:



The aromatic amino compounds which may be used as developing agents in the present invention include the mono-di and tri-amino aryl compounds. Among the mono-amino developing agents may be mentioned amino-phenols and amino-cresols and their halogen derivatives and amino-naphthols.

The developing agents mostly used and giving the best results in connection with the present invention are the aromatic ortho and para diamines, such as para-phenylenediamine and its substitution products. These developing agents may be substituted in one amino group or in the ring or in both, forming compounds such as:

Diethyl para phenylenediamine
Monoethyl para phenylenediamine
Dimethyl para phenylenediamine
3 amino-6 dimethylamino toluene.

These compounds are usually kept in the salt form such as hydrochloride or sulphate.

The following developer solutions may be used to give a colored image according to the present invention:

Formula 1

(A) Para-phenylenediamine HCl	g--	3
Sodium sulphite	g--	10
Sodium carbonate	g--	30
Sodium hydroxide	g--	2
Water	ccm--	1000

- (B) 4-(2'hydroxy,3',5' dibromobenzyl) 2 methyl 6 brom phenol 2 g.

For use, B is added to A.

Formula 2

(A) Dimethyl-paraphenylenedi- amine HCl	g--	3
Sodium sulphite	g--	7
Sodium carbonate	g--	25
Sodium hydroxide	g--	3
Water	ccm--	1000

- (B) 4-(2'hydroxy,3'-5' dibromobenzyl)-2 methoxyphenol g-- 2
Acetone ccm-- 25

For use, B is added to A.

Organic solvents for instance acetone or the like may be used to dissolve the color coupler.

The invention is in no way limited to the use of the color coupler in the developing solution itself. One of the essential products the color coupler which, during the development form the dye, can also be added to the photographic emulsion (for instance by absorption upon the silver salts) before or after coating. The other ingredients of the color forming baths, containing chiefly the aromatic amino developing agent, may be applied later, during the developing process, as a bath.

The present invention may be utilized in the formation of colored photographic images on plates or papers as well as on film employing gelatine or other carrier for the silver halide. The developing process may be used for the developing of photographic material, provided with one or more light sensitive layers, which are applied on one side or on both sides of the support.

The silver formed during the developing process may be eliminated. For this purpose a bath must be used, however, which does not destroy the dye. A bath consisting of a solution in water of potassium ferricyanide and sodium thiosulphate easily eliminates the silver without destroying the dye, leaving a pure dye image.

The new color couplers have decided advantages when compared with those known hitherto. They can be produced easily and they form with para-amino developers blue and blue/green dyes which are practically insoluble in water and in photographic baths. Their principal and most surprising quality is that their capacity of absorption is very small in the blue and blue/green part of the visible spectrum. They have, furthermore, the interesting property that, if added direct to the developing bath without being previously dissolved in organic solvents, they give intense coloration.

We claim:

1. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X=a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

2. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



10 where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

3. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = a naphthyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

4. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and at least one H-atom of the residue substituted by an individual included in the group alkyl aryl aralkyl alkoxy amino or nitro halogens and hydroxyl.

5. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = a phenyl residue with one hydroxyl group in a position para with regard to CH₂ and at least one of the remaining H-atoms of the residue substituted by an OH group.

6. Color forming developer comprising an aromatic amine developing agent and a color coupler

consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two bromine atoms

X' = an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

7. Color forming developer comprising an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two bromine atoms

X' = a phenyl residue with one hydroxyl group in a position para with regard to CH₂ and at least one of the remaining H-atoms of the residue substituted by an OH group.

8. Color forming developer comprising an aromatic amine developing agent which is a compound of the aromatic diamine group and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

9. Color forming developer comprising an aromatic amine developing agent which is a substituted phenylene diamine and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' = an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH₂.

10. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

X = a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH₂ and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

X' =an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 .

11. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

- X' =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 .

12. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



- where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

- X' =a naphthyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 .

13. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

- X' =an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and at least one H-atom of the residue substituted by an individual included in the group alkyl aryl aralkyl alkoxy amino or nitro halogens and hydroxyl.

14. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two halogen atoms

- X' =a phenyl residue with one hydroxyl group in a position para with regard to CH_2 and at least one of the remaining H-atoms of the residue substituted by an OH group.

15. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two bromine atoms

- X' =an aryl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 .

16. The process of color development of photographic material containing a developable silver salt image which comprises subjecting the image to the action of a color forming developer containing an aromatic amine developing agent and a color coupler consisting of a diaryl methane having the following general formula:



where

- X =a phenyl residue with one hydroxyl group in a position other than the meta position with regard to CH_2 and where at least two of the remaining H-atoms in the ring are replaced by two bromine atoms

- X' =a phenyl residue with one hydroxyl group in a position para with regard to CH_2 and at least one of the remaining H-atoms of the residue substituted by an OH group.

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