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PRODUCTION OF COLORED PHOTOGRAPHIC IMAGES BY COLOR DEVELOPMENT

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The invention relates to the production of colored photographic images by color development.

It is known that a colored image may be formed simultaneously with the silver image obtained by developing an exposed silver halide emulsion if a substance known as a "color former" is employed, for example, if the color former is mixed with the developer or incorporated in the emulsion. The colored image may be revealed by bleaching out the silver image with, for example, Farmer's reducer or another known photographic bleaching agent.

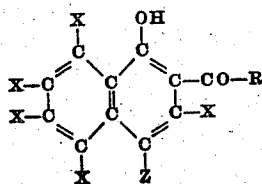
It is an object of this invention to provide a new range of color formers. A further object of the invention is to provide a method of producing colored photographic images with the aid of such color formers and a still further object is to provide light sensitive silver halide photographic materials containing the new color formers.

Other objects of the invention will appear hereinafter.

According to the invention a process for the production of colored photographic images comprises developing a reducible silver salt image with an aromatic amino compound as the developer in the presence of a color former which is a 2-acyl-1-naphthol in which the 2 substituent consists of a carboxylic acyl group and in which the total substituents on the naphthalene nucleus contain between them at least three carbon atoms. The 4-position in the naphthalene nucleus may be unsubstituted or may be substituted by a halogen atom.

The acyl group may be represented by the formula $R-CO-$, and R in this formula may be any hydrocarbon or substituted hydrocarbon radical. Thus R may be an alkyl group (preferably containing up to six carbon atoms), a substituted alkyl group, an aryl group, e. g. a phenyl or naphthyl group, a substituted aryl group, an aralkyl group, e. g. a benzyl group, or a substituted aralkyl group. Substituents in the alkyl, aryl, or aralkyl group may be, for example, chlorine or bromine atoms or nitro, hydroxy, alkoxy, amino and substituted amino groups, the substituted alkyl, aryl, or aralkyl groups being preferably linked by one of their carbon atoms to the carbonyl group.

The new color formers, therefore, are compounds of the following general formula:



in which R represents an alkyl group, preferably containing up to six carbon atoms, a substituted alkyl group, an aryl group, a substituted aryl group, an aralkyl group or a substituted aralkyl group linked by a carbon atom to the carbonyl group, Z represents a hydrogen atom or a halogen atom and the various X's, which may be the same or different, represent hydrogen atoms, halogen atoms or any monovalent substituent groups, e. g. alkyl, aryl, aralkyl, amino, substituted amino, hydroxy, alkoxy, nitro, sulphonic acid or acyl groups, the group $CO-R$ and one of the X's containing between them at least three carbon atoms.

The compound 2-acetyl-1-naphthol, which since it does not contain 3 carbon atoms in substituent groups is not included in the present invention, is also capable of acting as a color former. However, this compound is very sensitive to the presence of sulphites such as are commonly included in developers to inhibit aerial oxidation. The color formers included in the present invention have, in general, a satisfactory resistance to the action of sulphites and may be employed in conjunction with developers containing sulphites.

The developers used for developing colored photographic images with the aid of the color formers of the present invention do not, of course, necessarily contain sulphite, and where the risk of oxidation of the developer is not a material factor, sulphites may be omitted.

As indicated above, a wide range of 2-acyl-1-naphthols is included in the present invention. Thus, for example, simple 2-acyl-1-naphthols which contain no other substituent (i. e. where Z and all the X's of the above formula are hydrogen atoms and R contains at least two carbon atoms) are very suitable; examples are 2-acyl-1-naphthols in which the acyl groups are the following: n-propionyl, n-butyryl, iso-butyryl, n-valeryl, iso-valeryl, trimethylacetyl, caproyl, and heptoyl, oenanthoyl, pelargonyl, lauryl, myristyl, palmityl, stearyl, benzoyl, phenylacetyl, phenylpropionyl and cinnamoyl.

Again, the 2-acyl-1-naphthols may contain substituent groups in the positions of X and Z in the above general formula. Thus, a very satisfactory color former of the type where Z is a halogen atom is 2-propionyl-4-brom-1-naphthol.

Again, the color formers may be of the type wherein one or more of the X's in the above formula are monovalent substituent groups, e. g. 2:6-di-acetyl 1:5-dihydroxy naphthalene and 2:6-di-n-butyryl 1:5-dihydroxynaphthalene.

Also included in the present invention are acyl-naphthols in which two naphthol residues are linked by the residue of a dibasic acid such as

succinic acid or adipic acid. An example of this type is 2:2'-succinoyl-1:1'-dinaphthol.

Suitable aromatic amino compounds which may be employed as the developers in conjunction with the color-formers of this invention are derivatives of p-phenylene-diamine and particularly the asymmetric dialkyl p-phenylenediamines, e. g. p-aminodimethylaniline, p-amino-diethylaniline and p-aminodibutylaniline. Other developing agents which may be used include p-phenylenediamine itself, p-methylaminoaniline, p-ethylaminoaniline and p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethylamino-toluene, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine, 2-amino-5-hydroxyethyl-butyl-aminotoluene and its dihydrochloride and α - γ -dihydroxypropyl-p-phenylene diamine. These aromatic amino-developing agents may be used in the form of their salts, which may be either inorganic or organic. The salts are in general more stable than the free bases. As examples of suitable salts mention is made of the hydrochlorides, sulfates and acetates.

The color formers may be mixed with the developer or incorporated in the emulsion. A specific example of a suitable developing solution is as follows:

DEVELOPING SOLUTION-A

Di-ethyl-p-phenylene diamine hydrochloride	gm	1
Sodium carbonate crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	gms.	80
Sodium sulphite crystals, $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	gms.	12.5
Color former (1% or a saturated solution at room temperature in alcohol, whichever is the weaker)	ccs.	100
Distilled water to make	litre	1

If desired, the sodium sulphite may be omitted, its function being to fortify the solution against oxidation.

Exposed photographic emulsions developed in developers containing these compounds give dye images in varying shades of blue and blue-green and these dye images remain in the gelatin layer after removal of the silver image by treatment with, for example, Farmer's reducer.

In tests carried out with such developing solutions the time of development was two minutes at 65° F. but in many cases there were indications to show that this time was more than sufficient to produce the dye image required.

The following specific examples illustrate the use of the color formers as additions to photographic emulsions:

Example 1

Fifty ccs. of a melted photographic emulsion containing essentially silver bromide in the proportion of 40 gms. of silver halide per kilogram were mixed with a previously prepared mixture of 25 ccs. of a 10% gelatin solution and 25 ccs. of a 1% ethyl alcohol solution of 2-propionyl-1-naphthol, and the emulsion was coated on paper in the usual way. Test pieces of this coated paper were then exposed under a standard test negative and then developed for two minutes at 65° F. in the above developing solution-A but using equivalent ethyl alcohol in place of the color former solution, when a blue-green dye-

image was formed in association with the silver image, and the dye-image remained in the gelatin layer on removal of the silver image by treatment with Farmer's reducer.

Example 2

Fifty ccs. of a melted photographic emulsion containing essentially silver chloride in the proportion of 20 gms. of silver halide per kilogram of emulsion were mixed with a previously prepared mixture of 25 ccs. of a 10% gelatin solution and 20 ccs. of a 1% ethyl alcohol solution of 2-iso-butyryl-1-naphthol. This emulsion was then coated upon paper and test pieces of the coated paper were exposed under a test negative and developed for 2 minutes at 65° F. in developing solution-A but using equivalent ethyl alcohol in place of the color-former solution.

A deep blue-green dye-image was produced in association with the silver image and the dye-image remained in the gelatin layer after removal of the silver image by treatment with Farmer's reducer.

Instead of the specific color-formers named in the foregoing examples there may be employed in a similar manner, 2-phenylacetyl-1-naphthol, 2-cinnamoyl-1-naphthol, or 2:6 diacetyl 1:5 dihydroxy-naphthalene.

The 2-acyl-1-naphthols may be produced by reacting a 1-naphthol which is unsubstituted in the 2-position with an organic acid or organic acid anhydride in the presence of zinc chloride at a temperature between 160 and 200° C. at atmospheric pressure. When a polybasic acid is employed it is possible that the product will consist wholly or partly of a compound in which there is more than one naphthol nucleus. The use of such products is included within the process of the present invention.

The process of development employing the color-formers in accordance with the present invention may be applied either to a latent image in an emulsion of a silver halide which has been exposed to the action of light, for example, in a camera or behind a photographic negative image; or it may be applied to the residual unaltered silver halide left when an initial reduced silver image has been dissolved away as in the reversal process of development; or it may be applied to a developed photographic image in metallic silver which has been fixed by the removal of unaltered silver halide by means of solvents and subsequently converted to a developable silver salt by means of known photographic bleaching agents. In the last two cases, the residual silver halide and the silver salt respectively may be made developable by the action of light or in any other way, e. g. by treatment with sodium arsenite.

We claim:

1. The method which comprises developing a photographic element containing a reducible silver salt image with an aromatic amino developing compound in the presence of an acyl naphthol comprising two naphthol radicals linked by the diacyl radical of an aliphatic dibasic carboxylic acid.

2. The method which comprises developing a photographic element containing a reducible silver halide image with an arylenediamino developing agent in the presence of an acyl naphthol comprising two naphthol radicals linked by the diacyl radical of an aliphatic dibasic carboxylic acid.

3. A method as set forth in claim 2 wherein the acyl naphthol is 2:2'-succinoyl-1:1'-dinaphthol.
4. A method as set forth in claim 2 wherein the acyl naphthol is 2:2'-adipoyl-1:1'-dinaphthol.
5. A light sensitive silver halide photographic emulsion containing as a color former an acyl naphthol, comprising two naphthol radicals linked by the diacyl radical of an aliphatic dibasic carboxylic acid.
6. An emulsion as set forth in claim 5 wherein the acyl naphthol is 2:2'-succinoyl-1:1'-dinaphthol.
7. An emulsion as set forth in claim 5 wherein the acyl naphthol is 2:2'-adipoyl-1:1'-dinaphthol.
8. A photographic developer solution comprising an aromatic amino developing compound and an acyl naphthol comprising two naphthol radicals linked by the diacyl radical of an aliphatic dibasic carboxylic acid.
9. A photographic developer solution comprising an aromatic amino developing compound and 2:2'-succinoyl-1:1'-dinaphthol.
10. A photographic developer solution comprising an aromatic amino developing compound and 2:2'-adipoyl-1:1'-dinaphthol.

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