

# UNITED STATES PATENT OFFICE

2,206,126

## PHOTOGRAPHIC COLOR DEVELOPER

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No Drawing. Application April 29, 1937, Serial  
No. 139,758. In Austria May 9, 1936

4 Claims. (Cl. 95—88)

This invention relates to color photography, and particularly to methods of developing photographic images in colors.

In color photography, the latent image formed by exposure may be developed to a colored image, usually a dye image, which absorbs certain light rays and appears as a colored image by transmitted or reflected light. The colored image may be formed in various ways by treatment of the latent image, and the purpose of the present invention is to provide novel methods for producing colored images in photographic layers.

In one of the well-known prior art methods, in which the oxidation product of an ordinary developing agent, formed on development, couples with a color-forming compound, the colored images produced are not always clear, due to the condensation or oxidation of several molecules of the developer. I have found that this objectionable feature may be overcome to a large extent by using an excess of coupling component in the developer solution. The developing solution, consisting of a 1 to 2% solution of the developing agent, should contain 3 to 5 times the amount of coupling component theoretically required to couple with the developer, as well as sodium carbonate, trisodium phosphate, borax, sodium bicarbonate, sodium glycooll, etc., in addition to the ammonia or other alkali necessary for the solution of the phenol or naphthol couplers.

I have found, however, that the most favorable results in three-color reversal and redevelopment are obtained with simple color developers which are oxidized to the insoluble, or at least non-diffusing, dye by the exposed silver halide or that made developable in any other manner, as by bleaching to a halide after development. Two main groups are included: (A) Those in which two equal molecules of the developer are combined to the dye, that is, auto-couplers. (B) Those which can be regarded as leuco-form of the final image dye, and which transform into it by oxidation.

### A. Auto-coupling developers

The indophenol-similar dimer yellow quinone imide dye prepared by Auwers from o-aminosymm.m-xylenol belongs to the first group (Ber. 54/1291-1314; Fortschr. der ch., Phys. and phys. Ch. Bd. 18/Heft 2, page 1-45, 1924). Even the first experiments showed that a weak aqueous solution containing sodium carbonate yielded intensely lemon-yellow images, unless the exposure was too weak. The p-chlor- and p-brom-derivative also develop with formation of the lemon-

yellow quinone imide, but only slightly with the p-cyano-derivative also examined. Since the new dye is completely stable to acids and alkalies and is insoluble in lye, a 1-2% alkaline solution of this o-amino-phenol can serve as developer. Addition of sulfite is unnecessary, as the solution can be easily preserved. The rapidity of reaction can be increased, if in addition to the fixed alkali absolutely necessary for solution, also sodium carbonate is added or the developing solution is prepared at once with an excess of ammonia. A dilute alcoholic solution could, of course, also be used for development. The p-halide derivatives seem to develop somewhat more rapidly. P-amino-m-xylenol suggested and very useful as a developer does not seem to produce color images, although its alkaline solution precipitates a yellow dye after some time. Numerous other o-amino-phenols in alkaline solution, constructed analogous to the Auwer dye, are suitable as developers, as for example, o-amino-m-brom-m-cresol, which produces reddish-yellow images. Similar images also are produced by o-amino-m-xylenol while the o-amino-isopseudocumenol which is unfortunately very difficult to prepare yields brilliant lemon-yellow images. Red to purple color images may be obtained with different chlor and brom-derivatives of o-aminophenol, and other m-substituted o-aminophenols as: 3-methoxy-o-aminophenol, o-amino-resorcin-monoalkyl ether and the analogous resorcline derivatives, as well as with m-hydroxy-p-amino-dialkylaniline. Even the simplest o-amino-phenol yields reddish-yellow to orange images with development in a solution containing sodium carbonate or alkali, according to the dispersity of the dye or of the original silver halide. Homologues producing mostly red images are better suited, as for example o-amino-m-cresol in a solution containing sodium carbonate, or its brom-derivative, as well as 6-amino-cresol. It is very interesting that o-methylaminophenol and o-ethylamino-phenol, less satisfactory as developers, yield o-phenoxazine quinones by alkaline oxidation. Amidol is also said to yield red-brown dye images (Photographische Korrespondenz 1896/6,344). Experiments, however, showed that they were too weak; diamido-o-cresol behaves similarly. Numerous other quinone imides are formed during development with the corresponding diamino phenols or amino hydroquinones. Simple aminophenols and also aromatic p- or o-diamines are less inclined to precipitate insoluble oxidation products.

Among the heterocyclic compounds as for ex-

ample, the yellow carbazol quinone and its quinone imide which are formed in ammoniacal solution during development, one must take only the amount of lye, or rather ammonia, which is theoretically required for solution of the carbazol-aminophenol or -hydroquinone, if one expects vigorous color images.

$\beta$ -amino- $\alpha$ -naphthol forms violet images during development, 1-phenyl-amino- $\beta$ -naphthol forms reddish-yellow part images, and 4-phenyl-amino- $\alpha$ -naphthol develops to red images in alkaline solution. It is of greatest theoretical interest that also 3-phenylamino- $\alpha$ -naphthol develops to a purple color image, provided the sample used is not made impure by the presence of isomers. 4-amino-1: 2-dihydroxy-naphthalene yielding in development the red 2-hydroxy- $\alpha$ -naphthoquinoneimide (hydroximidonaphthol) and diamionaphthols of different constitutions are less suitable.

Formation of a yellow dye during development with the mono-carboxylic acid of 1:4-dihydroxy-naphthalene is an exception.

*Lignone dyes.*—Blue to purple lignones can be considered as analogues of the indigoid dyes. Their simplest representative is diphenoquinone which cannot be obtained by development. It is, however, rather easy to prepare their substitution products by oxidation of two molecules of the corresponding generators by means of the exposed silver halide. It was found that the long known orange-yellow coerulignone is produced not only during development with an alkaline solution of pyrogallol dimethylether, but also in development with hydrocoerulignone, and that a red-yellow image also remains after removal of the silver with Farmer's solution. The alkaline or ammoniacal solution of pyrogallol dimethylether is remarkably stable in comparison with that of hydrocoerulignone; it is not atmospheric oxygen, but the exposed silver halide alone, which effects the formation of the lignone dye. Similarly colored images at least with well-exposed silver chloride, are formed by vic.m-xylene. These orange-yellow tones are, however, of less importance in color photography.

Purple-red lignones are formed in development with oo-dichlor-, dibrom- and also diiodine-phenol probably only in alkaline solution, although these dihalide phenols are also soluble in sodium carbonate. It is interesting that also two molecules of tri-iodine phenol can be condensed by alkaline oxidation agents to tetra-iodine diphenoquinone.  $\alpha$ -naphthols substituted in the 2- and 4-position can very easily be combined to lignone dyes. Monoalkyl ether of 1,4-dihydroxy-naphthalene ( $\alpha$ -naphthhydroquinone) produces an intensely blue color image after development of the latent image in alkaline solution and removal of the silver formed by Farmer's reducer; the image consists of the so-called Russig dye. 2-mono-alkyl ether of 1:2-dihydroxy-naphthalene, however, easily prepared from the 1-diazo-derivative by exposure, yields a purple-red image. The mono-ethers of 1:4-dihydroxy-anthracene form a green dye image during photographic development, the mono-ethers of 1,2-dihydroxy-anthracene a more brick-red image.

The presence of alkoxy-groups in the 2- or 4-position of  $\alpha$ -naphthol is by no means a necessary condition for the formation of lignone dyes during development. It appears that any group is sufficient which cannot easily be reduced, among which are the phenyl residue, because 2-phenyl- $\alpha$ -naphthol yields purple part images in alkaline

developer solution, whereas its tetra-methoxy-derivative, easily prepared from papaverine, peculiarly forms a blue lignone dye.

The relatively high stability of the lignone generators in solution prepared with the theoretically required amount of alkali or ammonia seems to justify synthetic preparation of further representatives of this class of dyes.

Principally, the mono-ethers of the 1:4- or 1:2-dihydroxy-derivatives can be prepared from other higher aromatic ring systems, possibly with a heterocyclic ring attached, also of those in which a ring, not substituted by lignone-forming groups, is entirely or partially hydrated; this especially holds true for anthracene. The developing ability remains intact, if alkoxylation of one hydroxyl is not accomplished by methyl- or ethyl residues, but by higher aliphatic alcohols, benzyl- or phenyl-ethyl alcohol etc., also by phenyl and other aryls. Esterification can be accomplished by first allowing ethylene oxide to react in the required amounts with one hydroxyl group, followed by esterification of the hydroxyl groups in the hydroxyl-alkyl ether by means of the chlorides of aliphatic or aromatic acids in the presence of tertiary bases; if necessary, the aromatic hydroxyl group is first converted into the easily split carbethoxy-derivative. It is often better to attain this object in other ways, for example by substitution of the halide in the 4-brom- or 2-brom- $\alpha$ -naphthol by the phenol residue with sodium phenol in the presence of copper bronze. One can allow p-toluol sulfochloride to act on the ethers by 4-amino- $\alpha$ -naphthol in the presence of tertiary bases or other agents, whereby an arylsulfonylamine group of the same character as aromatic hydroxyl is formed. Red images are formed during development in alkaline or sodium carbonate solution. The analogous derivative of 2-alkoxy- $\alpha$ -naphthylamine yields violet-red color images. If the aromatic hydroxyl group is already alkoxyated by the hydroxyethyl residue, esterification of the aliphatic hydroxyl group and arylsulfonylation of the amino group can be accomplished together by using an excess of p-toluol sulfochloride. Amino- and hydroxyl groups can be introduced into the phenyl residue or the second nucleus of 2-phenyl- $\alpha$ -naphthol or also the monoethers of 1:2- and 1:4-dihydroxy-naphthalene mentioned, and this can be combined by acylation, alkylation, arylation and other synthetic operations with the different aromatic or heterocyclic systems. This is often connected with a far-reaching change of the color, as can be seen by comparison with lignons from 2-phenyl- $\alpha$ -naphthol and its tetra-methoxy derivative.

*Generators of indigoid dyes.*—Genuine vat dyes are often considerably superior to the lignones in stability, and many of them can be generated by condensation through oxidation of two equal molecules of their generators during photographic development. The generator is dissolved in the amount of lye or ammonia theoretically required, if necessary, mixed with an excess of sodium carbonate, unless it is soluble in sodium carbonate or water. More or less alcohol or sodium carbonate can also be added, or alkaline solutions of alcohol and acetone can be used. Since vat dyes do not add sulfite, any amount of it can be added to the developing solution, without special action, however, also sodium bromide can be added as needed. Fog-free images are only obtained, if working is done without atmospheric oxygen.

An almost unlimited number of generators is available or can be synthesized theoretically for the production of blue, green-blue and purple vat dyes in this manner; nevertheless, the choice of suitable yellow developers is very limited, that is, a true lemon-yellow developer is not available at all, unless barbituric acid is considered as generator of the lemon-yellow intermediate form of the so-called urindigo. Cumaranone in aqueous sodium carbonate solution, unfortunately, does not yield the lemon-yellow images corresponding to hydroxindigo. The carbindigo formed during development with a sodium carbonate solution of 4-hydroxyiso-carbostyryl is colored strongly red-yellow, if it is finely divided in gelatine, in the substance it is a pronounced red. The practically considered simplest generators (indoxyl, thioindoxyl, hydroxyseleno-naphthene) are somewhat soluble in water, and therefore, aqueous solutions containing sodium carbonate can be used for development. Solutions of their carboxylic acids containing sodium carbonate, or their neutral salts are more suitable, because they are much more stable than their alkaline solutions, except that of hydroxy-seleno-naphthene which is remarkably stable also in alkaline solutions, coloring only weakly red. The purple color of selenindigo almost corresponds to the theoretically required, not substituted thio-indigo, and correspondingly substituted indoxyls can be used in development for obtaining of green-blue indigos. The corresponding naphthalene (thio) indoxyls yield naphthene indigos, and naphthalene thioindoxyls of the same shade. The red-violet tone of 6,6'-dihalide indigos formed in development with the correspondingly substituted indoxyls are of practical importance because then the use of hydroxy-seleno-naphthene or substituted thioindigo for the formation of the purple part image appears unnecessary, and no reduction of the dyes formed previously in the other layers is to be feared.

Also the N-alkyl- and aryl-derivatives of indoxyl, its N-acyl derivatives, phenylthioindoxyl and its nitro- and amino derivatives, phenylhydroxythiophene are much more stable in alkaline or sodium carbonate solution than indoxyl and thioindoxyl, so that they are more suited for photographic purposes, even if the purity of the indigos formed has not yet been proven. Alkaline solutions of o-mercapto-acetophenone are still more stable, although it is gradually oxidized to thioindigo by atmospheric oxygen; it is, therefore, also worth considering as red developer. Some of the (thio) indoxyls derived from anthraquinone and benzathrone excel for their stability. Also sulfurylindoxyl is difficult to oxidize to sulfurylindigo similarly pyrindoxyl and thio-pyridindoxyl.

#### B. Leuco dye developers

**Quinone dyes.**—Substituted hydroquinone and naphthhydroquinones belonging to the second class are analogous to the leuco-forms of genuine vat dyes. Many among them are of the theoretically required lemon-yellow color. Of course, only those are considered which are converted into a completely insoluble quinone during development oxidation, while a certain solubility in water is desirable with the corresponding hydroquinone, so that it may also be used in sodium carbonate solutions.

The principal yellow developers are the multiple-arylated hydroquinones in alkaline solution, as 2:5-diphenyl-3:6-dibenzyl-hydroquinone,

2:5-dixylyl-hydroquinone, 2:5-di-p-tolyl-hydroquinone, 2:5-di-p-phenetyl-hydroquinone. Octahydrogenated anthrahydroquinones, easily prepared in small amounts by Skita, deserve special attention, and especially the  $\beta$ -methyl-derivative soluble in alkali, for the production of yellow dye images which can also be obtained with the hydrogenation product of 1:4-anthraquinone. The effect of a  $\beta$ -stable amino group changing the color of the hydrogenated quinone to red, is noteworthy. It is best developed in dilute alcoholic solution according to Glaisen. One could, of course, also here return through acylation of the amino group to the original color of the non-substituted quinone or to a still more suitable color. Similarly partially hydrogenated higher quinones can also be obtained by combination of unsaturated hydrocarbons with naphthoquinones and anthraquinones. Also 2-phenyl- $\alpha$ -naphthol-hydroquinone, diphenoxy-hydroquinone and many others yield yellow images.

Many of the numerous free and acylated, alkylated or arylated amino-, hydroxy-, mercapto derivatives, etc., of benzo- and naphthoquinones, as well as of higher quinones also with heterocyclic rings attached and mentioned in literature, are useful in color photography. The corresponding hydroquinones have been prepared from most of them, in as much as the latter could not be obtained with the formerly-used reducing agents, on account of their low stability, this is now accomplished in most cases by catalytic reduction in a properly selected medium. If acylation, alkylation, arylation etc. of the substituted groups has not been done at the beginning, it may sometimes also be accomplished in the finished quinone in order to prevent the simultaneous action on the hydroxyl groups of hydroquinone.

The free, possibly alkylated or arylated, not acylated amino-hydroquinones, etc., are only seldom so stable that they can be used for development in solution containing sodium carbonate or alkali, unless atmospheric oxygen is excluded, not considering the fact that also the amino quinones formed sometimes are inclined to polymerization with formation of blackish products. Also for the acylamino hydroquinones which are in themselves stabler, one must only take the amount of alkali just necessary for solution in order to prevent attacking of the gelatine. This sometimes seems to make the use of ammonia necessary. In the naphthalene group often those aminohydroquinones excel by greater stability in which the substitution is in the second nucleus. While o-quinones of the benzol series are only seldom easily prepared,  $\beta$ -naphthoquinones can be formed during photographic development, if the 4-position of 1:2-dihydroxy-naphthalene is fixed by alkyl-, aryl-, acyl-, acylamino-, ketone groups, etc., so that the great tendency to formation of 2-hydroxy- $\alpha$ -naphtho-quinone (hydroximinonaphtho) is stopped.

For example, the amino- and acylamino hydroquinones among which are phenyldiamino-hydroquinone, phenylmethyl-iminazol- $\beta$ -naphtholquinone also 4-acetamino-1:2-dihydroxy-naphthalene, 2-acetamino-3-chlor-1:4-dihydroxynaphthalene, 2:8-diacetamino-1:4-dihydroxynaphthalene, 2:5-diacetaminohydroquinone, etc., are especially noteworthy.

The brominated hydroquinones, such as adurol, also tri and tetra-chloroquinone, are suitable for synthetic preparation. Phenolate, naphtholate, p-toluol-sodium sulfamide, etc., are allowed to act

on them in the presence of copper bronze then they are reduced, if necessary. In this manner, yellow, blue to purple substitution products were obtained from thymoquinone. The condensation products with malonic ester, etc., are also worth mentioning further dichlor- $\alpha$ -naphtho-quinone with thioindoxyl and amines and similar condensation products of which the yellow naphthiminazolquinone from 2-amino-3-chlor-1:4-naphthoquinone is valuable.

The lemon-yellow  $\alpha$ -naphthoquinone diphenylmethane and the corresponding benzoquinone derivative is photographically valuable. Purple images are formed by the reduced condensation product from  $\alpha$ -naphthoquinone and Michler's hydrol. The reduction products of the dyes suggested for vat dyeing from *p*-hydroxyazines or acridine dyes with halogenated quinones among which also yellow developers are found, are included here. Also azine diquinones of lemon-yellow color are known as well as hydroxazine-o-quinones.

The red azo dyes or arylhydrazones from 1:2-dihydroxy-naphthalene, whose deep-blue alkaline solutions yield lemon-yellow 4-arylaazo- $\beta$ -naphthoquinone in the development of the latent image, are in a group by themselves. In conclusion it is mentioned that hydrazo forms of  $\alpha$ -naphthol azo dyes could be prepared in individual cases and also serve as developers. The reduction can often be accomplished without splitting of the azo group by catalysis with palladium and hydrogen at ordinary temperature and higher pressure, also with o-azodyes.

*Leuco vat dyes as developers.*—The leuco-indophenols which in many respects belong here, as well as leuco-indamines and leuco-azomethines may be sufficiently stable in alkaline solution to serve as developers, the finished dyes are, however, rather easily decomposed by acids. Also the reduced lignone dyes of the type of hydrocoerullignone or of the hydrated Russig dye are difficult to handle on account of the strong inclination to reoxidize the dye by atmospheric oxygen and the tendency to fog resulting from it. Jacobson, in his detailed investigation of the most favorable working conditions with hydrocoerullignone and 4-hydroxy-isocarboxystyryl (Atelier des Photographen 1929/86-89), recognized that these substances are a little suitable for practical color development as indoxyl, thioindoxyl, etc.

This criticism must, however, not be generalized, either in regard to the leuco-bodies concerned, or to the type of test conditions. Even tetra-chlor- and tetra-brom-diphenols are dissolved without color in lye or sodium carbonate, a sign of their indifference to atmospheric oxygen, and they yield fog-free purple color images in development. It is peculiar that the reduction product of tetra-iodine-diphenolquinone, easily obtained from tri-iodine phenol by alkaline oxidizing agents, is insoluble in lye. The leuco-form of the lignone from two molecules of tetra-methoxy-phenyl- $\alpha$ -naphthol in less degree of tetra-methyl-diphenolquinone and of their analogues, are similarly stable.

The leuco-forms of the genuine vat dye used in vat dyeing are very easily reoxidized in alkaline solution. Pure thioindigo white and selenoindigo white can be preserved for a long time. Indigo white is less durable, a dilute alcoholic solution of the same is immediately dehydrated to indigo by platinum-black, also anthrahydroquinone, of course, with absolute exclusion of

oxygen. Among the indigoid and analogous vat dyes there are much more stable leuco-derivatives, as: NN'-dimethyl indigo white of certain highly-halogenated thio-indigos, if they are reduced in the presence of too little alkali, or of those which form difficultly soluble alkali salts, as is the case with dinaphthacridonequinone with anthraquinonethioxanthenes and other anthraquinone dyes, tetra-hydroflaventhrene and its red dimethoxy, as well as the green acylamino, derivatives dihydrophen-anthridine yellow and its golden-yellow dimethyl derivative. Thionyl indigo white which is oxidized to the dye only by hydrogen peroxide and alkali, NN'-diphenyl indigo white, NN'-dimethyl indigo white, 2:2'-dibenzoyl thioindigo white, leuco-pyrindigo, the lemon-yellow diisobarbituric acid from 5-amino-uracile, the hydrated dinaphthacene diquinone, diamino-binaphthylene dioxide, the completely or partially reduced dibenzothianthrene diquinone dihalide-perylene-2:10-hydroquinones, dibenzoylamino-9:10-perylene hydroquinone are especially stable. Many amino-anthraquinones, also acylated ones or those with heterocyclic rings attached, or substituted by alkoxy- or arylhydroxyl- or acylhydroxy-groups, are reduced by many reducing agents or catalytically to the anthranol or anthrone form. It was found that not only the derivatives of anthrahydroquinone, but also those of the anthranol form are capable of developing the latent image. If the reduced dye is in its anthrone form, it is converted into the alkaline salt of the anthranol form by warming with lye or, if necessary, by addition of alcohol, and the anthranol form is used for development. Images of the lemon-yellow dianthrone are obtained with the salt of dianthrone. Tetrahydro-helianthrone is constructed very analogously and to tetranhydroxy-helianthrone. The leuco-forms of the condensation products from two molecules of indoxyl, thio-indoxyl, hydroxy-selenonaphthene, etc., with one molecule of an aliphatic, also unsaturated or aromatic dialdehyde are somewhat stabler than those of the genuine indigo dyes.

Until now it was questionable, whether indigo white, and with it leuco-vat dyes, have developing power at all. Liesegang 1895 stated that indigo white (or its sulfonic acid, Jahrb. f. Ph. 1896/487) is able to produce a strong black image and also Abribat confirmed this later, but Lumiere and Seyewetz found that it must be ascribed to an impurity of hydrosulfite or ferrosulfate. None of these authors has investigated, whether indigo is also formed.

It could be determined that indigo white, thioindigo white and selenoindigo white are really developers. It is, however, necessary to work without atmospheric oxygen, since otherwise a general blue fog is developed. Another condition is that very much potassium bromide or at least 2% potassium iodide must be added to the developer, if moderately clear images are to be expected. The very finely divided indigo is reduced in a test tube with aqueous alkaline hydrosulfite solution on which a layer of benzol or petroleum several centimeters high is poured. The exposed film is covered by a protecting sheet which is removed only after passing the petroleum layer, otherwise development hardly takes place. Nobody will deny that such a developing method is inconvenient for the amateur and the professional. But in motion-picture technique where the film is developed by automatic machines, this difficulty is easily overcome, allowing air-sensitive

substances to be used for color photography. The air in the developing apparatus is replaced by nitrogen or any other indifferent gas, also illuminating gas may be used in case of emergency, or the apparatus is installed in a room filled with such a gas and the operator must wear a gas mask with air supply. This method of working is not only recommended when using leuco-vat dyes, indoxyl, thioindoxyl, etc., or hydrated quinone dyes, but also in the usual black development of motion picture films, since by this method large quantities of valuable developer substance and sulfite are saved which otherwise are lost by oxidation from the air. It is understood that in color development with vat dyes and for washing, boiled or distilled water should be used, in order to avoid color fog. The preparation of vat solutions or other air-sensitive developing solutions is, of course, also done without oxygen, after which it is filtered and placed in the developing machine. As little hydrosulfite as possible should be used; the excess can be converted by addition of formaldehyde or better non-tanning aldehydes into Rongalite or similar substances which cannot be developed any more. This is not absolutely necessary, since also in the presence of hydrosulfite sufficiently strong color images are formed. This method of working is also advisable in the production of colored images by means of coupling developers, as for example,  $\alpha$ -naphthol and p-amido-dimethylaniline, in order to avoid color fog. It is sometimes recommended not only to fill the developing apparatus with inert gas, but also to cover the solutions with a layer of petroleum or other liquids which do not attack the film.

Alkaline or possibly ammoniacal solutions of the vat dyes are usually considered for the formation of the last, as a rule middle, image only, because most of them reduce unexposed silver halide also, unless very much potassium bromide or a few percent potassium iodide are added to the developer. The principal method of making silver halide emulsions developable is, of course, by thiourea, etc., or reducing to silver ferrocyanide. For colored development of the two other emulsions vat solutions are usable, since in indoxyl and its derivatives and analogues easier generation of the vat dyes is available. Also here, 1-2% solutions are used.

When using leuco-vat dyes and their generators, one should consider that some of them in alkaline solutions have the ability to reduce the dye already formed on the image. Alkaline indigo white solutions, for example, or vat dyes formed on warming of halogenated indigo or thioindigo which is even capable of reducing itself to the leuco form may be used. Color development of the exposed silver halide usually takes place much more quickly than the action on the vat dye already present. This difficulty is entirely avoided, if the vat solution with weaker reduction potential is used last for development. The middle part image is formed with the vat solution of a highly halogenated indigoid dye, which contains no excess alkali or at the most only sodium carbonate. When the lower part image has developed to indigo or more greenish derivatives of the same, the middle image can be developed purple with the aid of the red- to red-violet 6,6'-dihalide indigo or its leuco-form.

Ammonia is recommended to use for the solution of the vat dye, because this does not attack the gelatine, even with a slight excess, as much as fixed alkali does. Alcohol or acetone in any

amount may also be added to aqueous solution in addition to alkali or ammonia in the theoretically required amount, unless the film is harmed by it. Alkali-free solutions of the leuco-forms can be used for development of the last emulsion in alcohol or acetone with addition of aliphatic amines, ethylene diamine, piperidine, etc. In opposite order of the emulsions, the green-blue or purple part image of the upper emulsion can also be developed by an aqueous suspension of indigo white or thioindigo white, which are dissolved in small amounts; if necessary, this may be used after addition of potash or sodium carbonate. In this case, also the relatively stable, even if difficultly soluble, magnesium salts of leuco vat dyes can be used for development as also the difficultly soluble alkali salts of the various highly halogenated indigo and thioindigo dyes, and of some higher molecular vat dyes. Also purely aqueous suspensions or solutions of the leuco forms in alcohol or acetone reduce silver chloride made developable by exposure, or by thiourea, through prolonged action with absolute exclusion of atmospheric oxygen, or after addition of aromatic amines.

It may happen that the dye formed in the color development is not entirely insoluble in water, but at the same time so persistently adsorbed by the silver formed, that it cannot diffuse away. In these cases it is advisable before removal of the silver with Farmer's solution, to treat with precipitants in order to obtain water-proof part images. For weakly basic indophenols or indamines formed by coupling with p-aminodimethylaniline etc., phosphotungstic acid and its analogues or their salts, and for dyes of acid nature, inorganic or organic bases are used. This is, however, unnecessary with  $\alpha$ -naphthol blue, so that for exposure of the middle emulsion all silver of the lower emulsion can be first removed without harm.

In the U. S. Pat. 1,076,301 it is stated that in each color development of the latent image the emulsion is not completely developed out, but a residue is left behind which reacts to a certain degree with the next color developer, so that wrong color effects are produced. It was found that this is not the case with a triple layer and perfectly correct colors are obtained, if each part image is developed sufficiently long, if necessary, with addition of potassium bromide, or with a fresh developer, or by finishing development with an ordinary black developer which has no coupling ability and also cannot contain sulfite, if indophenol or azomethine dyes are used. After washing, the next color development is done. In order to be absolutely sure, one could also bathe in potassium ferricyanide after each part color development, but only for such a short time that only the residues of the previous latent image are destroyed, the reduced silver, however, not essentially attacked. Since careful washing of all traces of ferricyanide is necessary in order to avoid color fog, and also occasionally the (color) sensitivity must be regenerated by a following bath of sulfite, bisulfite, hydrazine or hydroxylamine etc., the whole color process is retarded and made more expensive.

The color developers must not necessarily be pure, but may also contain other non-color-developing or coupling developer substances in order to reduce the intensity of the color image and to obtain the correct gradation in respect to the other part color images, by the relation of the

rapidity of both developers in this mixture or to the coupling tendency of the one.

In reversal development, it is recommended to use those primary developers which do not form desensitizing oxidation products, since these do not always remain on the place of their origin, but also are capable of diffusing. This effects later exposures of residual or regenerated silver halide in the same or adjacent emulsion. Iron oxalate developer of normal composition is well suitable. The general opinion that a residual image of such developer oxidation products is indispensable in the formation of correctly graduated reversal images, does at least not apply for the triple layer with its thin layers of silver bromide gelatine. For this reason it is also recommended to use a large excess of components in the coupling developers, so that no desensitizing oxidation products are formed from the developer substance.

For development in an indifferent atmosphere, also those amino-hydroxy-derivatives, especially of the naphthalene series, are suitable, which on account of their color fog are considered neither for ordinary, nor for color development. Since dimer quinone imide dyes are, according to Auwer, very resistant not only to acids, but also to reducing agents, they can serve for the production of the yellow and also of the purple lower part image, while the middle image is formed by direct development with a strongly acting leuco-vat dye. In films coated on both sides, two leuco-vat dyes can be used independently from each other, one for each side, while the third part color image is developed with another color developer. If the triple layer contains a silver chloride emulsion, the second color development can also be done with a vat solution, if the silver chloride remaining from the preceding development has been converted into the more resistant silver ferrocyanide; in reversal and redevelopment it can then be reduced to the last part color image by a strong leuco-vat dye, either directly or after reconversion into silver chloride.

If the triple layer is intended for printing, the middle layer alone must be sensitized for yellow or red, and it is preferably surrounded by two layers absorbing ultra-violet or the outer silver halide emulsion prepared with these substances. Very transparent and fine-grain emulsions can be used here, and all three or at least the middle layer can consist of silver chloride. In contact printing or optical printing of three-color images, uniform gradation can be obtained by the use of different color filters or variation of the exposure. In black part negatives, one prints first with colored light on the sensitized middle layer and then with ultra-violet light on the two other layers.

Several possibilities for recording negative or positive sound in variable density or variable width exist. With white light, one can print on

all three layers, so that it finally appears black, or it is printed on only one or two layers and developed in color and then exposed to complementary light for reproduction. The photo cell must, however be sensitive to this light. In order to protect the sound strip against damage, it is best to print it in the lower emulsion. This is especially advantageous in reverse order of the layers where the blue-sensitive layer adjoining the support consists of highly dispersed sensitized silver halide and the following yellow filter acts as antihalation, if one prints with blue light. Besides, in a normal triple layer, a fourth, approximately grainless, silver halide emulsion could be arranged which is sensitized for infra-red, so that printing and developing take place independently from the others. Printing is done optically through the back, if the anti-halation layer is transparent to infra-red. Printing can be done after drying also in any stage of the coloring process. The sound strip can be arranged as in modern processes as multiple variable width, as combination of the variable density and variable width, etc.

It is to be understood that I consider the various modifications and examples of the foregoing specification, whether claimed or not, as included within the scope of my invention; and I desire to secure by Letters Patent of the United States, protection on all the novel subject matter disclosed herein.

I claim:

1. A photographic developer comprising a compound selected from the group consisting of 1:2 dihydroxy anthracene compounds, 1:4 dihydroxy anthracene compounds, and alkyl monoethers of 1:2 and 1:4 dihydroxy anthracene in a weakly alkaline solution, the developer being capable of forming a colored image in an exposed gelatino-silver halide emulsion layer.

2. A photographic developer comprising a compound selected from the group consisting of 1:2 dihydroxy anthracene compounds, 1:4 dihydroxy anthracene compounds, and alkyl monoethers of 1:2 and 1:4 dihydroxy anthracene in a 1 to 2% solution of an alkali, the developer being capable of forming a colored image in an exposed gelatino-silver halide emulsion layer.

3. A photographic developer comprising an alkyl ether of a dihydroxy anthracene selected from the group consisting of 1:2 and 1:4-dihydroxy-anthracenes in a weakly alkaline solution, the developer being capable of forming a colored image in an exposed gelatino-silver halide emulsion layer.

4. A photographic developer comprising an alkyl ether of a dihydroxy anthracene selected from the group consisting of 1:2 and 1:4-dihydroxy-anthracenes in a 1 to 2% solution of an alkali, the developer being capable of forming a colored image in an exposed gelatino-silver halide emulsion layer.

KARL SCHINZEL.