

# UNITED STATES PATENT OFFICE

2,297,732

## PHOTOGRAPHIC COLOR PROCESS INVOLVING THE FORMATION OF AZO DYE IMAGES

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This invention relates to color photography, and more particularly to methods for obtaining colored photographic images in stable dyes. Still more particularly it relates to procedures for producing azo dye images in photographic elements involving the use of immobile color formers and a novel combination of chemical reactions.

At the present time there are two principal methods for the direct production of subtractive three-color photographic pictures bearing dye images. One of these involves the use of multilayer films which are processed by controlled bleaching and color development steps to colored images in azomethine and quinoneimine dyes. The other utilizes a multilayer film the layers of which contain insoluble or at least nonmigratory dye coupling components, the image-bearing film being processed by a single color development to azomethine and quinoneimine dyes. The basic principle of color development used in both processes employs an aromatic amine-type developing agent containing an unsubstituted amino group, generally an aminodialkylaniline, according to a procedure developed many years ago by Fischer, see for instance, U. S. Patents 1,055,155 and 1,102,028. These processes may be said to be quite successful but suffer the disadvantage that the resulting dyes are fugitive to light, moisture, and traces of acid. Further, the colors that can be produced by this method are more or less limited and in many cases lack desirable brilliance. Many attempts have been made to produce colored images in the much superior azo dyes, but the processes are quite complicated and expensive.

The present invention is based on the fact that many coupling components will form mutually exclusive colored products with both the photographic oxidation products of photographic color developers and with diazo compounds, and while the former are easily decolorizable without removing them from the film element, the latter are stable under conditions which cause decolorization of the former. Since the primary condensation products are formed only in the areas where silver is produced by development, azo dyes can therefore be produced only in the areas where no reduction of silver salts to silver by color development has occurred.

This invention has for an object the production of images in azo dyes. A further object is the production of a plurality of images in azo dyes of different colors in a multilayer film on a suitable support. A further object is to provide a simple process for producing azo dye images in film elements containing reducible silver salts and immobile color formers subsequent to color development of such elements. A still further object is to provide a method of producing images in different azo dyes simultaneously in a plurality of layers containing immobile color formers capable of reaction with diazonium compounds and which have been partially converted to temporary dye images during color development. Other objects will appear hereinafter.

The above disadvantages are overcome and the objects attained by the following invention in which a developed film element bearing at least one immobile dye intermediate, as hereinafter defined, which intermediate or intermediates have been in part converted to one or more temporary dyes by reaction with the photographic oxidation products of a color developing agent during the development step, is subjected to the steps comprising coupling of the unconverted dye intermediate with diazonium compounds and bleaching of the temporary dyes produced in the development step to colorless products which remain in the film. The silver is bleached and the silver salts are removed at any suitable time subsequent to color development.

More specifically, color-developed photographic elements bearing at least one immobile dye intermediate containing a coupling group which has been converted into azomethine, or quinoneimine dyes including indophenol, indoaniline and indamine dyes in latent image areas are subjected to the steps comprising coupling of the unconverted dye intermediate with diazonium compounds and bleaching of the temporary developed colors to colorless products which remain in the film. The silver can be bleached and the silver salts can be removed at any time subsequent to color development.

In the broad aspects of the invention just described, the immobile dye intermediates are converted to temporary dyes of the above-mentioned type in the latent image areas during color development of the film bearing latent

images or developable silver salts. These temporary dyes are incapable of reacting with diazonium compounds but may be decolorized under conditions which do not remove them from the film element. The film element, either before the temporary dyes have been decolorized or afterward, is placed in a solution containing a diazonium compound which will couple with the unconverted dye intermediates to form azo dye images in the areas where no color development occurred. Thus, when the silver and silver salts have been removed, a colored picture in azo dyes remains.

In carrying out the embodiment of the invention just described, natural color photographs, containing only azo dyes and the colorless product or products formed from the temporary dyes, are prepared by use of a multilayer film containing three different immobile dye intermediates. These intermediates must be of the type which are capable of being coupled with diazotized amines to form azo dyes of the three subtractive primary colors, namely, yellow, magenta, and blue-green, and which have each been in part converted to color developed temporary dye images, that is, in areas commensurate with the silver image formed by color development of suitably sensitized and exposed photographic emulsions. The film containing these intermediates and temporary dyes is treated by the steps consisting of azo dye coupling of the unconverted intermediates and decolorization of the temporary color developed dyes.

The photographic elements and especially the films used in carrying out the invention are similar to those employed in various types of multi-color photography and may vary considerably in structure. For instance, a film element can be prepared bearing three differently sensitized silver salt emulsions and suitably colored filter layers so that each emulsion will record approximately one-third of the visible spectrum. In addition, each emulsion layer contains an immobile dye intermediate which will form a temporary dye on color development and which can be converted to an azo dye complementary to the color recorded in the emulsion stratum or layer-containing it. Such a film can be exposed to a natural color scene, can be printed with white light through a color record or transparency, can be printed with colored light from suitable color separation records, etc. This exposed film can then be either developed with a color-forming developing agent, aromatic primary amine developing agents, for example, are commonly used, or it can be developed in a non-color-forming developer, fixed, and the silver bleached to reducible silver salts which are then developed in the color-forming developer.

In an alternative embodiment, a film such as that just described may be exposed to a natural color transparency or printed from color separation records, developed in a non-color-forming developer, exposed or chemically fogged, and the residual silver salts developed in a color-forming developer, to form temporary dyes in the regions originally unexposed. During this color development, a part of the immobile dye intermediates is coupled with the oxidation products of the color-forming aromatic amino developing agents at the points of development in known manner to form azomethine or quinoneimine dyes which are incapable of reacting with diazonium compounds and which are not removed from the film but can be converted to colorless products. The color of

these azomethine or quinoneimine dyes is unimportant since the dyes are subsequently bleached.

Films color-developed according to the above procedure can, after the developer has been washed out, be exposed to light, if desired, during their further processing to azo dye images. Such processing, as previously stated, consists of two essential steps: (1) reacting with a diazonium compound to form azo dye images, and (2) decolorizing of the formed azomethine or quinoneimine dyes in which types are also included indo-phenol, indoaniline or indamine dyes. The order in which this step is carried out is immaterial. Thus, when the temporary dye is easily bleached by solutions that have no effect on the azo dye, decolorization can be subsequent to azo dye formation, but when the temporary dyes require more vigorous reagents for decolorization, then it is advisable to convert them to colorless products before azo dye formation. When the film resulting from completion of steps (1) and (2) has been treated to remove silver and silver salts, which latter process can occur prior or subsequent to the azo dye forming steps, it will contain colored images in azo dyes and colorless derivatives of the temporary dye coupling products.

By immobile dye intermediate is meant a compound in the colloidal state, soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate solution at 25° C., which contains in its molecule an acidic salt-forming group or a salt thereof, which is capable (1) of forming a quinoneimine or azomethine dye and (2) of forming an azo dye. The preferred compounds of this type are readily soluble in 5% aqueous sodium carbonate solutions and in many cases are soluble in water alone. It has been found that the ready solubility of these immobile dye intermediates in mildly alkaline solutions offers important advantages. Thus, in contradistinction to products soluble only in caustic alkalis, as, for example, sodium hydroxide, or to the insoluble pigment type of dye intermediate, the products of the present invention are highly compatible with gelatino-silver halide emulsions and lead to the preparation of clear, transparent films. Another important advantage is that the soluble products of this invention are converted to bright and brilliant dyes, while it has been found that relatively insoluble types referred to above, lead to dull and muddy colors. The acidic salt-forming groups which contribute to the good solubility in mildly alkaline reagents are preferably carboxyl or sulfonic acid groups but may be phosphate. Since the photographic emulsion is usually weakly alkaline and very sensitive to major changes in its alkalinity, it is customary to convert the immobile dye intermediate to its alkali metal, ammonium, or lower aliphatic amine salt before incorporation in the emulsion.

These dye intermediates, being colloidal in nature, are not removed from the film element by aqueous processing solutions and are proof against migration in or between emulsion layers during any of the processing steps. To obtain good reproduction and clear images, the immobile dye intermediate should not be convertible to products which are migratory in the carrying agent or which can be washed out by aqueous processing baths. Such conversion to migratory products would occur if the intermediates were subject (1) to hydrolysis or splitting in photographic processing baths which will not destroy or injure the carrying agent of the emulsion, (2)

to condensation and coupling to give soluble products with other components such as the oxidation products of amino developing agents containing carboxylic or sulfonic acid groups or with diazotized aminosulfonic or carboxylic acids. The types of immobile dye intermediates found to be especially useful and which are preferred include:

1. Mixed polyvinyl acetals of aldehydes containing coupling component nuclei and of aldehydes containing solubilizing groups. These acetals are formed from polyvinyl alcohol or from polyvinyl alcohol derivatives containing free hydroxyl groups such as partially hydrolyzed polyvinyl esters. The polyvinyl alcohols are reacted with both mono- or polynuclear aromatic aldehydes which contain a phenolic hydroxyl (in addition they may contain an unsubstituted amino, or an alkyl-, cycloalkyl-, or aryl-substituted amino group) and with aldehydes containing carboxyl or sulfonic acid groups. These coupling components are further characterized in that they have a reactive position but not necessarily an unsubstituted position ortho or para to the mentioned groups. Aromatic aldehydes having an active methylene group may also be used. The preparation of suitable compounds of this type is set forth in Dorough & McQueen application, Serial No. 233,480, filed October 5, 1938.

2. Condensation products of hydroxy aromatic carboxylic or sulfonic acids with bifunctional resin-forming reagents, for example, aldehydes and ketones, dimethylol derivatives of phenols, of amides, or of amines, and of equivalent compounds. The preparation of suitable color-formers of this type is described in McQueen application, Serial No. 261,794, filed March 14, 1939.

3. Condensation products of amine-containing dye intermediates, with polycarboxylic acids or with their derivatives such as the anhydrides, esters, halides, or amides. Polymeric acids of this type and their derivatives include the polyvinyl ethers of hydroxy acids, olefin-maleic anhydride interpolymers, polyacrylic acid, polymeric olefin dicarboxylic esters and interpolymers of esters of olefin dicarboxylic acids with vinyl esters and styrene as described in U. S. Patent 1,945,307. Amine containing dye intermediates of this type include aminophenols, aminonaphthols, N-aminoalkyl- or N-aminoaryl-aminonaphthols, amine-containing active methylene compounds such as aminoaroyl- or aminoacyl-acetanilides, aminophenylmethyl pyrazolones, or any of these compounds containing solubilizing groups such as carboxyl or sulfonic acid groups.

4. Immobile dye intermediates from N-mono- and di-alkylated or aralkylated aminonaphthols containing in a side chain a group capable of further condensation such as an amine group which intermediates are formed by condensing the aminonaphthols with a polymeric acid or derivative thereof as listed above in paragraph 3.

Specific color formers of the above type are set forth below and described in the working examples.

Practically any diazo compound can be used with single layer film elements as long as they are reactive and form stable solutions for an appreciable length of time. Many different diazo compounds have been included in the working examples but it has been discovered that certain of these are particularly suited for use with multilayer film and must be employed if a complete color range is to be obtained. These diazo

compounds which constitute an important feature of the invention are (1) tetraazotized benzidine derivatives which can be substituted by nitro, halogen, alkoxy, alkyl, trifluoromethyl, and sulfonic acid groups, and (2) diazotized 4-nitroaniline derivatives wherein the 2-position can be substituted by one of the groups consisting of halogen, alkoxy, alkyl, trifluoromethyl, sulfonic acid, nitro and carboxylic acid groups and wherein the 6-position is occupied by one of the groups consisting of hydrogen, halogen, nitro, sulfonic, carboxyl, alkyl, haloalkyl, or alkoxy. The preferred compounds of this type are tetraazotized dianisidine, diazotized 2-chloro-4-nitroaniline and diazotized p-nitroaniline-o-sulfonic acid.

Another important aspect of the invention is the discovery that the diazo coupling gives better results if, following the preliminary color development to quinoneimine or azomethine dyes, the photographic element is placed in a cold solution of a diazotized amine, the pH of which is about 1 to 7 and preferably from about 3 to about 6. After the solution has thoroughly penetrated the emulsion layer or layers the element is placed in a weakly alkaline solution of a pH between about 7 and about 10 containing either ammonium hydroxide, an amine or an alkaline-reacting salt such as sodium acetate, sodium phosphate, or the like.

This procedure is especially useful with multilayer films and must be followed to obtain the proper colors, using the preferred types of coupling components of this invention. For instance, the preferred coupling components for producing blue-green azo dyes are derivatives of aminonaphthols which can couple in either acid or alkaline solutions. However, it is only when coupling proceeds in a solution whose pH is less than 7, that the coupling reaction is directed by the amino group and the proper shade of blue-green azo dye is produced. The coupling components used to produce the yellow and magenta dyes, on the other hand, react with diazonium compounds readily only in solutions whose pH is 7 or greater, (see Unit Processes in Organic Syntheses, Groggins, pp. 146-147). Hence, an important feature of the invention lies in the fact that it provides for coupling ortho or para to an amino group of one dye intermediate in an acidic bath, followed by coupling ortho or para to a hydroxyl group of another dye intermediate in an alkaline bath.

Novel bleaching procedures which convert the temporary coupling developed dyes to colorless products also constitute an important feature of the invention. Thus, before or after formation of the azo dye images the quinonemine or azomethine dyes and metallic silver images may be bleached simultaneously by treatment with an acidic solution of an oxidizing agent such as a cupric or ferric halide, a dichromate, a permanganate, etc., in preferably between 1 and 20% concentration, which solution is also capable of converting silver to silver salts and contains one to five per cent of an acid or has a pH of about 1 to about 6. Suitable acids include strong mineral acids, e. g. sulfuric, hydrochloric, phosphoric and nitric; acetic and sulfamic acids. Of these, sulfuric, hydrochloric, and sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) are preferred. Any residual undesired color may be destroyed by a subsequent rinse in a cold aqueous solution of a weakly alkaline salt such as sodium phosphate, etc., or ammonia or an amine and which solution contains about 0.5% of sodium hydrosulfite.

Among the useful oxidizing agents are cupric or ferric chlorides and bromides, sodium, potassium and ammonium permanganate and dichromate, ferric ammonium sulfate, ceric ammonium sulfate and ammonium persulfate. Of these, the cupric and ferric halides are preferred since they are mild in their action on photographic emulsions.

In certain cases where the temporary dyes are more stable and resist these methods of bleaching or tend to reappear in later steps, it is often desirable to use a strong reducing solution for decolorization. Such solutions may be alkaline solutions of pH between 7 and 11 and containing as reducing agents sodium hydrosulfite, sodium formaldehyde sulfoxylate, sodium and ammonium sulfide, hydrazine or hydroxylamine. Of these, sodium hydrosulfite and sodium formaldehyde sulfoxylate, are preferred. Acidic solutions containing any of the previously mentioned strong mineral acids also may be used where the pH is between 1 and 7 and which contain as reducing agents stannous chloride, cuprous and ferrous salts. When these reducing solutions are to be used, they should be employed prior to azo dye formation so that the azo dyes will not be adversely affected. It is often advantageous when using these solutions to remove the silver and silver salts first, and then to form the azo dyes after reducing the indophenol colors and thoroughly washing out the reducing solution. Films obtained in this manner have exceptionally clear high lights and bright clear dye images.

It is readily demonstrated that these temporary azomethine and quinoneimine dyes are not removed from the film but are merely converted to colorless products since when any of the films produced by this method are introduced into a weakly alkaline solution containing about 4% of potassium ferricyanide the temporary dyes are regenerated practically quantitatively.

The bleaching baths may contain beside the above-mentioned constituents, other agents such as retardants or materials to decrease or control the penetration of the baths, for example, ethyl alcohol, methyl alcohol, acetone, glucose; softening agents for the photographic film and emulsion such as glycerol, hardening agents, or inorganic salts with no specific or adverse effect on silver images or silver halides, such as sodium sulfate and sodium acetate.

The invention in all its novel and useful aspects can be better understood by a consideration of the following examples which are illustrative of the same, but not intended to limit it in any way and wherein the parts stated are parts by weight.

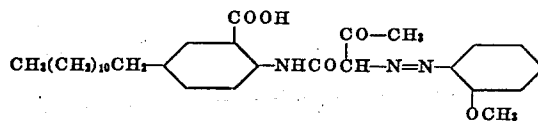
#### Example I

To 100 parts of a photosensitive gelatino-silver bromide emulsion containing approximately 10 to 15 per cent solids by weight is added 2 parts of p-dodecylacetoacet-o-carboxy-anilide, dissolved in 50 parts of 2 per cent sodium carbonate solution and the mixture coated on a subbed cellulose acetate film base, and dried. The film is exposed in a camera to a color field, or under a color transparency positive in case a print or duplicate is being made, then developed in the following solution:

	Parts
A. Sodium carbonate.....	20
Sodium sulfite.....	1
Water.....	500
B. p-Aminodiethylaniline hydrochloride.....	2
Water.....	483

Mix equal parts of A and B.

After development the film is washed and placed in a diazo solution prepared as follows: 6.15 parts of o-anisidine is dissolved in 125 parts of 1 molar hydrochloric acid and cooled to 2-4° C., then 10 parts of 5 molar sodium nitrite solution is added at 2-4° C., after 5 minutes the mixture is diluted with ice water to 1900 parts; then 110 parts of 1 molar ammonium hydroxide solution is added and the solution kept at 5° C. After the film has been immersed in this solution for 30 seconds, it is removed and washed thoroughly. The film is next placed in a 5 per cent by weight aqueous copper bromide bleach bath containing 5 parts of concentrated hydrochloric acid per 100 parts of solution to oxidize the silver image and to bleach the temporary indophenol dyes. Next it is washed, immersed for 30 seconds in cold 1 per cent sodium hydroxide solution containing 0.1 per cent of sodium hydrosulfite, rinsed and fixed. The resulting film bears a positive image in the yellow azo dye of the following structure:



#### Example II

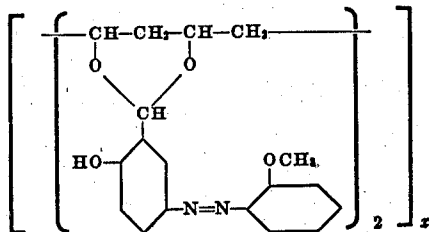
To 1000 parts of a photosensitive gelatino-silver bromide emulsion containing approximately 10 to 15 per cent solids by weight is added 24 parts of a polyvinyl acetal prepared from 2-hydroxybenzaldehyde, o-sulfobenzaldehyde and polyvinyl alcohol dissolved in 200 parts of 4 per cent sodium carbonate. This compound may be made as described in aforesaid Dorrough and McQueen application, Serial No. 233,480. The mixture is coated on a cellulose nitrate film base and dried. The film is then exposed to an original color scene and developed in the following solution:

	Parts
A. Sodium carbonate.....	20
Sodium sulfite.....	1
Water.....	500
B. p-Phenylenediamine hydrochloride.....	2
Water.....	483

Mix equal parts of A and B.

After development (the developing solution of Example I may also be used), and washing, the film is placed in a diazo solution prepared as follows: 6.1 parts of dianisidine is dissolved in 125 parts of boiling 1 molar hydrochloric acid and cooled to 2-4° C., then 10 parts of 5 molar sodium nitrite solution is added at 2-4° C. After 5 minutes, the mixture is filtered and diluted with ice water to 4000 parts. After the film has been immersed in this solution for 30 seconds, it is removed and immediately placed in a solution containing 3 per cent by weight of ammonia which has been cooled to 5° C. After remaining in this solution for 30 seconds, it is removed and thoroughly washed. The film is next placed in a solution prepared by dissolving first 10 parts of copper sulfate in 90 parts of water and then adding 5 parts of potassium bromide and 5 parts of concentrated hydrochloric acid. When the silver image has been completely oxidized, the film is removed, washed and fixed. The resulting

film bears a positive image in a yellow azo dye having the following probable unit structure:



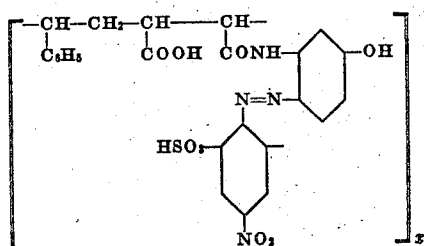
Example III

To 1000 parts of a photosensitive gelatino silver bromide emulsion containing approximately 10-15% solids by weight is added 100 parts of a 2% sodium carbonate solution containing 10 parts of a polymeric acid amide prepared by condensing equimolar portions of m-aminophenol and a styrenemaleic anhydride interpolymer. The mixture is coated on a cellulose nitrate film base and dried. The film is then exposed to an original color scene and developed in the following solution:

	Parts
A. Sodium carbonate	20
Sodium sulfite	1
Water	500
B. p-Aminophenol hydrochloride	2
Water	483

Mix equal parts of A and B.

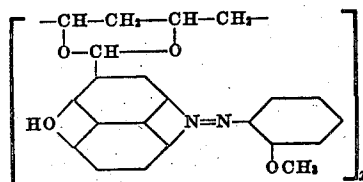
After development (the developer solutions of Examples I and II may be used) and washing, the film is placed in a solution prepared by dissolving first 10 parts of copper sulfate in 90 parts of water and then adding 5 parts of potassium bromide and 5 parts of concentrated hydrochloric acid used. The film is then washed and placed in a diazonium solution prepared as follows: 2.18 parts of p-nitroaniline-o-sulfonic acid is dissolved in 40 parts of 1% sodium hydroxide diluted with 200 parts of ice water and 50 parts of 1-molar hydrochloric acid, then cooled to 5° C. The solution is diazotized with 20 parts of 0.5 molar sodium nitrite solution, filtered, and diluted to 1000 parts with ice water. After the film has been immersed in this solution for 30 seconds, it is removed and placed in a solution containing 3% by weight of ammonia which has been cooled to 5° C. After remaining in this solution for 30 seconds, it is removed, thoroughly washed and fixed. The resulting film has a positive image in the yellow dye of the following probable color unit structure:



Example IV

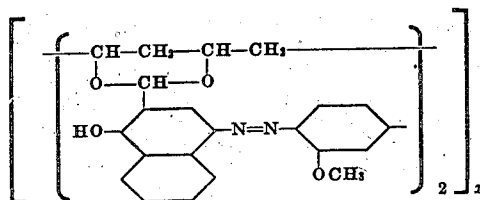
To 1000 parts of a photosensitive gelatino-silver bromide emulsion containing approximately 10-15 per cent solids by weight is added 250 parts of a 4 per cent sodium carbonate solution containing 30 parts of a polyvinyl acetal prepared from 1-hydroxy-2-naphthaldehyde and o-

sulfobenzaldehyde as described in aforesaid Dorough and McQueen application and the mixture coated on a cellulose acetate film base and dried. The film is then exposed and developed in a developing solution as described in Example I (the developing solutions of Examples II and III can also be used), and processed as the film in Example I after development. The resulting film bears a positive image in a red azo dye containing the following probable chromophoric unit:



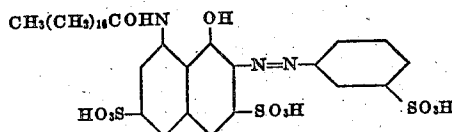
Example V

A photographic film prepared as in Example IV is processed as the film in Example II. The resulting film bears a positive image in a magenta azo dye which has the following probable color unit structure:



Example VI

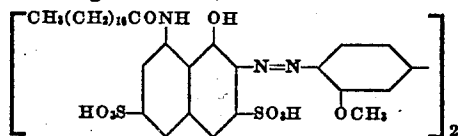
To 1000 parts of a photosensitive gelatino-silver halide emulsion containing approximately 10-15 per cent solids by weight is added 15 parts of 1-stearylamino-8-naphthol-3, 6-disulfonic acid dissolved in 100 parts of 2 per cent sodium carbonate solution. For the preparation of this dye intermediate, see British Patents 393,966 and 400,922. The emulsion is then coated on a cellulose acetate film base, dried, exposed, and developed as in Example I. (The developing solutions of Examples II or III can also be used.) The film after development and washing is then placed in a diazo solution prepared as follows: 10 parts of metanilic acid is dissolved in 125 parts of hot 1 molar hydrochloric acid and cooled to 2-4° C., to this is added 10 parts of 5 molar sodium nitrite solution at 2-4° C. After 5 minutes, the mixture is diluted with ice water to 1900 parts and then 100 parts of 5 molar ammonium hydroxide solution is added and it is kept at 5° C. After the film has been immersed in this solution for about 30 seconds, it is removed and washed thoroughly. The processing from this step is carried out as on the film in Example I. (The process of Examples II or III can also be used.) The resulting film bears a positive image in the magenta azo dye of the following structure:



Example VII

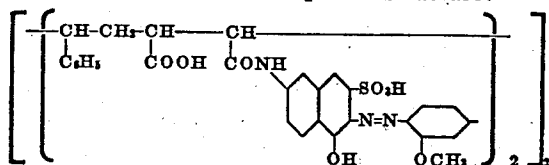
A film prepared as in Example VI is processed as the film in Example II. The resulting film

bears a positive image in the purple azo dye of the following structure:



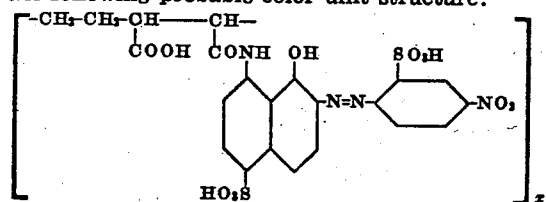
Example VIII

To 1000 parts of a photosensitive gelatin-silver bromide emulsion containing approximately 10-15% solids by weight is added 100 parts of an aqueous solution containing 10 parts of the neutral sodium salt of a polymeric carboxylic acid amide prepared by condensing a styrene-maleic anhydride interpolmer with 2-amino-5-naphthol-7-sulfonic acid. The emulsion is coated on a cellulose acetate film base and dried. The film is processed by the method described in Example II. The film bears a positive image in the magenta azo dye having the following probable chromophoric structure:



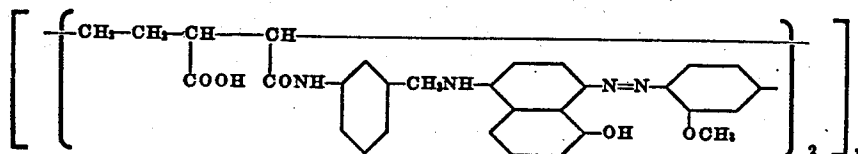
Example IX

A film is prepared according to the method of Example VIII using as the dye intermediate 12 grams of the neutral sodium salt of the condensation product of an ethylene-maleic anhydride interpolmer and 1-amino-8-naphthol-4-sulfonic acid. The film is processed by the method described in Example III. The resulting film bears a positive image in the orange azo dye which has the following probable color unit structure:



Example X

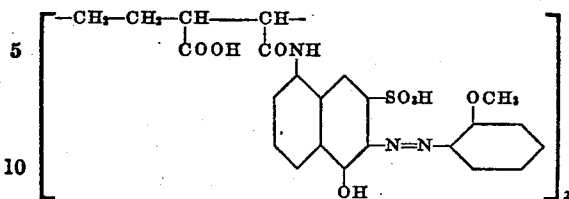
A film is prepared by the method described in



Example XII

Example VIII using as the dye intermediate 12 grams of the neutral sodium salt of the condensation product of an ethylene-maleic anhydride interpolmer and 1-amino-5-naphthol-7-sulfonic acid. The film is processed by the method described in Example I. The resulting film bears a positive

image in the red azo dye which has the following probable basic color structure:



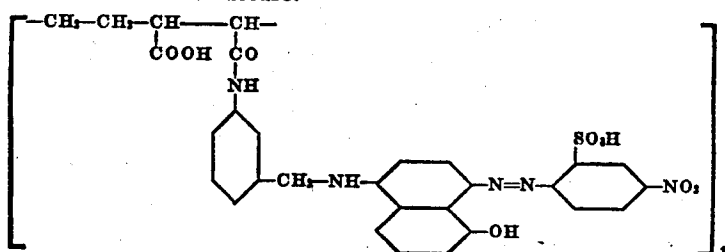
Example XI

To 1000 parts of a photosensitive gelatin-silver bromide emulsion containing approximately 10-15% solids by weight is added 100 parts of a 1% sodium carbonate solution containing 7 parts of a polymeric carboxylic acid amide prepared by condensing an ethylene-maleic anhydride polymer with 1-m-aminobenzylamino-5-naphthol. The emulsion is coated on the cellulose acetate film base and dried. The film is then exposed to an original color scene and developed in the following solution:

	Parts
A. Sodium carbonate.....	10
Sodium sulfite.....	2
Sodium hydroxide.....	8
Water.....	500
B. 5-aminosalicylic acid.....	3
Water.....	483

Mix equal parts of A and B.

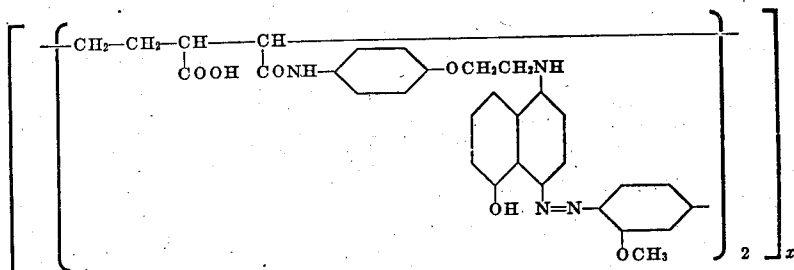
After development and washing, the film is placed in a copper bleach bath as described in Example II, then washed and fixed. The film is next placed in a 1% sodium hydroxide solution containing 5 parts of sodium hydrosulfite per 100 parts of solution. After remaining in this solution until the temporary dyes are completely bleached, the film is removed and washed in water for 10 minutes and placed in a diazonium solution prepared as in Example II. After remaining in this solution for about one minute, the film is removed and placed in a solution containing 3% by weight of ammonia which has been cooled to 5° C. The resulting film, after washing, bears a positive image in the blue azo dye containing the following probable chromophoric structure:



A film prepared as in Example XI is processed by the method described in Example XI using the diazonium solution of Example III. The resulting film bears a positive image in the blue-green azo dye of the following probable color unit structure.

*Example XIII*

A film is prepared as in Example XI using as the dye intermediate the condensation product of an ethylenemaleic anhydride polymer and 1-p-aminophenoxyethylamino - 5 - naphthol. The film is processed by a method described in Example XI. The resulting film bears a positive image in the blue-green azo dye of the following probable color unit structure:

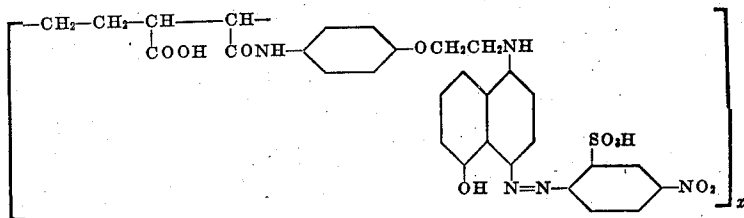


The emulsion is coated on a cellulose acetate film base and dried. This film may then be exposed and developed as in Example III. After development and washing, the film is placed in the diazo solution prepared as follows: 6.38 parts of p-chloro-aniline is dissolved in 125 parts of 1 molar hydrochloric acid and cooled to 2-4° C. To this is added 10 parts of 5 molar sodium nitrite solution at 2-4° C., and after 5 minutes the mixture is diluted with ice water to 4000 parts and

*Example XIV*

A film prepared as in Example XIII is processed by the method described in Example XII. The resulting film bears a positive image in the blue-green azo dye of the following probable chromophoric structure:

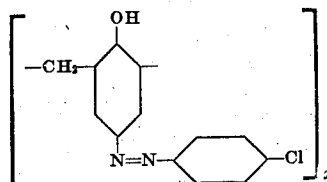
kept at 5° C. during use. After about 1 minute the film is removed and placed immediately in cold 5 per cent ammonium hydroxide solution for one minute, removed and washed thoroughly. This film is then bleached and fixed as is the film in either Examples I or II. The resulting film bears a positive image in a yellow azo dye



*Example XV*

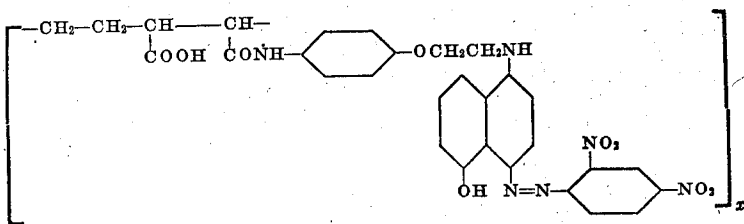
A film is prepared as in Example XIII and processed as in Example XI, except that the diazonium solution is prepared as follows: 1.83 parts of 2,4-dinitroaniline is dissolved in 10 parts of concentrated sulfuric acid and cooled to 5° C. To this is added a solution of 0.7 part of sodium nitrite in 5 parts of sulfuric acid. After 10 minutes the mixture is cautiously diluted with ice and water to 1000 parts and kept at 5° C. during use. The resulting film bears a positive image in the green azo dye of the following probable color unit structure:

having the following probable color unit structure:



*Example XVII*

To 250 parts of a photosensitive gelatino-silver bromide emulsion sensitized to the green region



*Example XVI*

To 100 parts of a photosensitive gelatino-silver bromide emulsion containing approximately 10-15 per cent solids by weight is added 8 parts of a p-hydroxybenzoic acid-formaldehyde resin dissolved in 100 parts of 2 per cent sodium carbonate solution. For preparation of this resin, see U. S. application McQueen, Serial No. 261,794.

of the spectrum is added 1.5 parts of stearyl-J-acid dissolved in 50 parts of 1% sodium carbonate solution. This is coated on a cellulose acetate film base, dried, and a second thin layer of clear gelatin is then coated on top of this. Next an emulsion prepared by adding 3 grams of a 3-allyl-2-hydroxy-benzaldehyde, o-sulfobenzaldehyde acetal of polyvinyl alcohol (prepared as de-

scribed in U. S. application Ser. No. 233,480 dissolved in 50 parts of 4% sodium carbonate solution to 250 grams of a photo-sensitive gelatino-silver halide emulsion sensitive only to blue light is coated on the film base. Tartrazine was added to this last emulsion just prior to coating to act as a yellow filter layer to prevent blue light from reaching the orthochromatic emulsion. This film was exposed with white light through a positive color transparency and processed as described in Example II. This film containing yellow and magenta azo dye images when placed in register with a positive blue-green record prepared by exposing the film of Example XIV to red light through the same color transparency, produced a positive photograph in natural colors.

#### Example XVIII

To 1000 parts of a photosensitive gelatino-silver bromide emulsion containing approximately 12-15% solids by weight and sensitized to record the red region of the spectrum is added 100 parts of 1% sodium carbonate solution containing 6 parts of a polymeric carboxylic acid amide prepared by condensing an ethylenemaleic anhydride polymer with 1-p-amino-phenoxyethylamino-5-naphthol. This is coated on a cellulose acetate film base and dried. On top of this is coated an emulsion prepared by adding to 1000 parts of a photosensitive gelatino-silver bromide emulsion sensitized to record the green region of the spectrum 10 parts of the neutral sodium salt of a polymeric carboxylic acid amide dissolved in 200 parts of water prepared by condensing a styrene-maleic anhydride polymer with 1,8-amino-naphthol-3,6-disulfonic acid. Above this is coated a thin gelatin layer containing tartrazine as a yellow filter dye. After drying, an emulsion sensitive only to blue light prepared as in Example II is coated above the yellow filter layer. The film is then exposed in any suitable manner as to a natural color scene with white light, through a color positive with white light, or with appropriately colored light through separation positive films. The film is then processed as in Example XII, allowing the film to remain a longer time in the various solutions to insure complete penetration. The resulting film contains a full color positive in azo dyes.

#### Example XIX

To 1000 parts of a photosensitive gelatino-silver halide emulsion containing approximately 12-15% solids by weight and sensitized to record the red-orange region of the spectrum is added 6 grams of the dye intermediate of Example XIII, and this is coated on a cellulose nitrate film base. Above this is coated a gelatin layer containing tartrazine as a yellow filter layer. Next, above this is coated an emulsion prepared by adding to 1000 parts of a photosensitive gelatino-silver halide emulsion, containing approximately 12-15% solids by weight and sensitized to record the blue-green region of the spectrum, 10 parts of the neutral sodium salt of a polymeric carboxylic acid amide prepared by condensing a styrene-maleic anhydride polymer with 1,5-amino-naphthol-7-sulfonic acid dissolved in 200 parts of water. This film is then exposed in any suitable manner as to a natural color scene illuminated with white light, through a color negative with white light, or with appropriately colored light through separation positive films. The film is then processed as in Example XVIII, giving

ing a natural color positive transparency in azo dyes.

#### Example XX

A film prepared as in any of the previous examples is exposed to an original color scene to form latent images in the emulsion layers and given a primary development in a non-coupling developer, i. e., one whose oxidation products do not react with the dye intermediates, it is then exposed to white light or chemically fogged and processed according to the methods described in the previous examples. The resulting film then contains a negative image in the corresponding azo dye or dyes.

#### Example XXI

A film as prepared in any of the Examples I to XVIII, inclusive, is exposed through separation negatives with appropriately colored lights to form latent images in the emulsion layers and treated as in Example XX. The resulting film then contains a positive image in the corresponding azo dye.

#### Example XXII

A film as prepared in any of the Examples I to XVIII, inclusive, is exposed to an original color scene, given a preliminary development in a non-coupling developer, i. e., one whose oxidation product did not react with the dye intermediate. It is then fixed and the silver reoxidized to an insoluble silver salt and processed according to the method described in the corresponding examples. The resulting film then contains a positive image in the corresponding azo dye or dyes.

The invention is not limited to the specific color formers or dye intermediates set forth above, but on the contrary, many other dye intermediates may be employed so long as they fulfill the requirements specified above. Thus, any practically colorless compound containing the common dye-forming nuclei known in the art and which may be found in any of the dye chemistry textbooks (see Pierz-David, *Kunstliche Organische Farb.*, pp. 78-204) may be used so long as they couple both with the oxidation products of photographic color developers to form decolorizable compounds not affected by diazo solutions and also to form azo dyes. Such nuclei are in general aromatic in nature and possess one or more of a number of different substituents, among which are phenolic hydroxyl, amine, alkylamine, dialkylamine, and arylamine. These nuclei, as is well known in the art, must also have ortho or para to the above directive substituent a hydrogen atom or readily replaceable group which will be eliminated in the coupling reaction. In place of one of these nuclei a compound possessing an active methylene group, i. e. a methylene group whose hydrogen atoms are sufficiently acidic or replaceable to couple or condense with a diazonium compound, may be employed.

The preferred immobile dye intermediates of this invention contain the following dye forming nuclei: (1) one or more aromatic nuclei, one of which is substituted with a phenolic hydroxyl group and has in the ortho or para position to the said phenolic hydroxyl group a hydrogen atom or group such as carboxyl, sulfonic acid or halogen which is easily replaceable (i. e. behaves like hydrogen in coupling reactions with diazo solutions or with the oxidation products of photographic color developers), (2) two or more aro-



matic nuclei fused together and substituted in one ring with a phenolic hydroxyl group and having in the ortho or para position to said hydroxyl group a hydrogen atom or removable group as defined above under (1), and having in an adjacent ring an amino group either primary, secondary or tertiary and having in the ortho or para position to said amino group a hydrogen atom or removable group as defined above under (1), (or the primary and secondary amino groups may be also acylated), and (3) compounds containing active methylene groups. These coupling nuclei also may be substituted by a host of varied substituents. For example, they may contain halogen atoms, primary-, secondary-, tertiary- or iso- alkyl, alkoxy, aralkyl, aryl, nitro, amido, carboxylic, or sulfonic acid groups, provided that a coupling position is available for the azo and photographic coupling reactions.

As examples of suitable alkyl groups which may be present in the above color formers are methyl, ethyl, propyl, isopropyl, butyl, octyl, dodecyl, octadecyl, etc. Suitable alkoxy groups include methoxy, ethoxy, dodecoxy, octadecoxy, etc. Suitable aralkyl groups include benzyl, tolyl, menaphthyl. Any of the halogens, fluorine, chlorine, bromine, and iodine, may be present; however, chlorine and bromine groups are preferred as substituents.

The immobilization of the dye intermediates may be effected in various ways. Long chain alkyl groups containing from 12 to 20 carbon atoms as substituents confer such properties. Alkyl ether groups and cycloalkyl ether groups of 8 to 20 or more carbon atoms as substituents have a similar effect. If amino groups are present they may be reacted to form amides of high molecular weight acids such as long chain fatty acids, naphthenic acids, resin acids, polymeric acids and the like. The compounds may be immobile because of their molecular weight, polymeric nature, structure or because of the presence of carbohydrate, polypeptide or sterol residues. Examples of this type are set forth above.

The condensation products of alpha halogen aromatic ketones with pyridine derivatives as set forth in U. S. Patent 2,154,918 have utility in the processes hereof, as do the long chain aliphatic ethers of polyhydric phenols of U. S. Patent 2,166,181, and the cycloaliphatic ethers of polyhydric phenols of U. S. Patent 2,189,817.

A large variety of developing agents may be used in processing the film elements used in this invention, provided they couple under conditions of development with the color formers and do not form dyes which are capable of further azo coupling. Thus, in place of the specific aromatic amino developing agents described in the preceding examples there may be substituted various other specific agents of this type. These agents have an unsubstituted amino group which apparently enables the oxidation product to couple with the color-forming compound. Such agents may be described as primary aromatic amino developing agents. These compounds having more than one amino group may be substituted in one amino group as well as in the ring. Thus, halogen, alkyl, alkoxy and aryl groups may be present.

The preferred developing agents in the process of dye coupling development are p-phenylenediamine, p-aminophenol and their derivatives. These include the asymmetric dialkyl p-phenylenediamines whose alkyl groups contain 1 to 4 carbon atoms, e. g. p-aminodimethylaniline, p-aminodiethylaniline, p-aminodibutylaniline, and

also p-aminophenyl carboxylic acid, p-aminophenol sulfonic acid, and 2,5-diamino-benzoic acid. Other developing agents which may be used include p-aminomethylaniline, p-aminoethylaniline, o-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 2,5-diaminotoluene, 2-amino-5-diethylaminotoluene, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine 2-amino-5-(N-butyl-N-hydroxyethyl) aminotoluene,  $\beta$ - $\gamma$ -dihydroxypropyl-p-phenylenediamine, etc. These aromatic amino developing agents in the form of their organic or inorganic acid salts may be used in the preparation of the developing solutions. The salts are in general more stable than the free bases. As examples of suitable salts mention is made of the hydrochloride, sulfates, acetates, etc.

Further examples of developing agents that can be used in this process are: heterocyclic compounds containing benzene nuclei such as 1, 2, 3, 4-tetrahydro-6-aminoquinoline, 1, 2, 3, 4-tetrahydro-6-amino-quinoxaline, etc. (British Patent 478,345); N-hydroxy-alkyl p-phenylenediamine (British Patent 460,580); halogenated p-aminophenols (French Patent 813,902); p-phenylenediamine derivatives containing solubilizing groups in the positive radical connected to the nitrogen atom (French Patent 822,269); and di-N-hydroxyalkyl p-phenylenediamine derivatives (U. S. Patent 2,108,243),  $\alpha$ -aminoacetoacetic acid ethyl ester, etc.

The diazo solutions used in preparing individual azo dyes may be prepared from many primary amines other than those used in the above examples. Amines which are suitable for diazotizing and coupling to azo dyes are well known in the art (see Fierz-David "Kunstliche Organische Farbstoffe" and J. C. Cain "The Chemistry of the Diazo Compounds," pages 6-26). These are in general of the type RNH<sub>2</sub> where R is aromatic or a heterocyclic ring such as pyridine, pyrazolone, etc. The R may also be substituted with various groups such as halogen, alkyl, alkoxy, aryl, sulfonic, carboxyl, nitro, etc. In choosing the amine to be used there are in general two considerations to be observed, (1) the diazo compound must be sufficiently active to couple readily with the dye intermediate used at a relatively low temperature and in aqueous solution; (2) the diazo compound must be one which can be coupled to yield bright azo dyes with spectral characteristics suitable for use in three-color photography, that is, they must have fairly definite and sharp absorption bands. Thus, the most suitable amines are those containing halogen, alkoxy, nitro, carboxy, and sulfonic acid groups.

For successful application of this process to 3-color photography it is necessary to have diazonium compounds that will couple with three colorless components to yield the three subtractive primary colors, yellow, magenta, and blue-green. Almost all diazotizable amines can be coupled with phenolic coupling components and active methylene compounds such as phenylmethylpyrazolone, acetoacetanilide and aroylacetanilides, etc., to yield greenish-yellow to orange-yellow azo dyes. The number of combinations that yield magenta dyes is greatly limited, since the coupling components to conform to the previously mentioned requirement must be substituted naphthols and naphthyl-

amines and only a limited number of diazonium compounds will condense with such components to form magenta colors. Thus, diazotized aniline derivatives usually yield a magenta color only when substituted in the ortho or para position with such groups as phenyl and nitro. Tetra-

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zotized diamino compounds such as benzidine and diamionaphthalene derivatives substituted with halogen, alkoxy, and sulfonic acid groups may also be used. In forming the blue-green azo color, the choice is further restricted since the best colorless coupling components which adhere to the previous qualifications are derivatives of 1, 5- and 1, 8-aminonaphthol in which the amino group is preferably secondary or tertiary, and must remain basic. The preferred diazotizable amines that can be used for forming all three colors therefore are substituted benzidine derivatives containing halogen, alkyl, nitro, carboxyl, alkoxy or sulfonic acid groups; and substituted para-nitroaniline derivatives containing in the 2 and/or 6 position hydrogen, halogen, alkoxy, nitro, carboxyl or sulfonic acid groups which all give desirable properties to the diazo components and to the dyes.

The azo coupling reaction may be carried out directly in the diazo solution if its pH has been adjusted so that coupling readily occurs therein (see Examples I and XI). Or if the pH of the diazo solution is too low to permit coupling, the film saturated with the diazo solution is placed in a bath of the proper pH to promote rapid coupling (see Example II). The choice of the best procedure depends on several factors. If the film contains dye intermediates all of which couple at the same pH and the diazo compound is soluble, stable, and reactive at this pH value, then the first method may be used. However, if the diazo body tends to precipitate, decompose, or change slowly to an inactive form at the pH most suitable for rapid coupling, then the second procedure may be used. In cases where the different dye coupling components couple at different pH values, it is desirable to use a diazo solution whose pH is the lowest of these values, and then after the first coupling has taken place, the film saturated with a diazonium compound is placed in a bath of the higher pH. Compounds suitable for adjusting the pH are inorganic acids such as hydrochloric, sulfuric, etc.; weak organic acids such as acetic, propionic, citric, etc.; basic salts such as alkali metal acetates, carbonates, phosphates; hydroxides such as alkali metal hydroxides, ammonium hydroxides, and aliphatic amines. It is also possible in such cases where the different coupling components react at different pH values to use different diazo components with them. Thus, such a film may be placed in a diazo solution whose pH value is low enough so that only one of the coupling components reacts. After complete reaction of this component the film is thoroughly washed and treated as in Example I or II to cause the other coupling components to react. Also, in cases where emulsions are coated on both sides of the film base it is possible to use different diazo solutions by allowing only one side at a time to come in contact with the coupling bath or baths.

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The steps involving bleaching of the silver image and decolorization of the temporary developer coupling product may be carried out together or separately either before or after azo dye formation. If they are to be carried out separately, the silver is bleached with a reagent such as 4 75

per cent potassium ferricyanide solution; following this the film is placed in cold 5 per cent mineral acid solution containing 1 to 10% of an oxidizing agent for 1-5 minutes, then rinsed in cold 1 per cent alkaline hydroxide solution containing 0.1 per cent of an alkaline hydrosulfite for one minute, washed and fixed. If the two bleaches are to be carried out simultaneously, an acid bleach is used. Such bleaches may be aqueous copper halide solutions containing between 1 and 10% of the halide, a 10 per cent copper sulfate solution containing 5 per cent of freshly dissolved potassium bromide, or an acid dichromate bleach, or any other commonly used photographic acid bleach. In any case, it is advisable after this bleach to rinse the film in cold 5 per cent mineral acid solution before washing and fixing. In cases where the temporary dye is difficult to decolorize a strong reducing agent may be employed as above described; such reducing solutions are preferably used subsequent to bleaching of the silver images and fixation. Using the latter type of bleach, it is usually desirable to bleach, fix and decolorize the film before the azo coupling step. In this case, the azo coupling reaction proceeds as before but on a transparent film containing no visible image, and the resulting film is the same in all cases.

Various types of silver halide emulsions may be used, e. g. silver chloride, silver bromide, and silver chloro-bromide, silver bromide-iodide, etc. emulsions. They may likewise be used in conjunction with the known sensitizing dyes which render the emulsions sensitive to certain additional wave-length regions of light. They may also be used in conjunction with emulsion desensitizers, surface modifiers and emulsion hardening agents. Various colloid binding agents may be used in the emulsion layers in place of the gelatin of the above examples, e. g. agar agar, cellulose derivatives, e. g. lower alkyl ethers and esters, glycollates, regenerated cellulose, synthetic resins, etc.

The products and process of this invention find wide application in color photography. Thus, if a photograph of a natural color scene is taken with a camera using a multilayer photographic film according to this invention, the final film will contain a positive image, and if the coupling components have been correctly chosen, the image will be a perfect color reproduction of the object photographed. Or if a primary development is made in a non-color-forming developer followed by re-exposure or chemical fogging and by color-forming development, the film may be processed to a color negative in which the colors are complementary to those of the object photographed. Transparencies prepared according to this invention may be used to make color prints or separation negatives, or to make duplicate copies of the original. Films prepared according to this invention may be used as printing mediums to make large numbers of color transparencies from color or separation records if these records are printed in registration and with the proper light sources. Single layer films may also be used to make color transparencies from separation records by printing each record on the single layer film containing the appropriate dye intermediate, color developing, processing, and assembling the three separate color records on a transparent or opaque support. Also, it is possible to place the three emulsion layers on a paper backing or a white support and use as a printing paper in making colored prints.

One outstanding advantage of this invention lies in the fact that azo dyes as a class are very much more stable than the dyes produced in other photographic processes, that is, they are more resistant to fading in strong light, or during long storage, and to the acidic degradation products generated in the film base during storage. This is an important factor to be considered when using films to make permanent records and pictures that are to be kept over long periods or are exposed to direct light for any length of time. Another important advantage is that azo dyes give a wider and more complete range of colors than any other type of dye and by proper choice of intermediates, dyes of superior photographic characteristics may be obtained, i. e., dyes with spectral curves close to the theoretical curves required for subtractive 3-color photography. Since after the first development, all further processing may be carried out in direct light, another important advantage of this invention consists of a more accurate control of the tonal values of the final color reproduction. These advantages, combined with the ease of processing films by this invention and simplicity of operation, make this a most attractive process for producing natural colors in photographic films and prints.

An advantage of the use of the novel immobile dye intermediates hereof resides in the fact that they may be completely and uniformly dispersed in the binding agents and emulsions. They are compatible with silver halide emulsions and being in a colloidal state, do not migrate. The insoluble types on the other hand do not give clear pictures.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments hereof, except as defined in the appended claims.

I claim:

1. A photographic color process which comprises exposing a photographic element bearing at least one light-sensitive silver halide emulsion layer containing an immobile dye intermediate capable of forming (1) a dye by color forming development and (2) an azo dye, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., color developing the exposed areas, forming an azo dye in the remaining areas, and bleaching the color developed dye images to colorless products which remain in said layer.

2. A photographic color process which comprises treating a developed photographic element, bearing at least one immobile dye intermediate, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., which intermediate has been in part converted to a dye taken from the class consisting of azomethine and quinoneimine dyes by coupling during development of silver salt images, with a solution containing diazonium compounds to couple with the unconverted dye intermediate, bleaching the dye formed during color development to colorless

products which remain in the element, and removing the silver and silver salts subsequent to development.

3. A photographic color process which comprises exposing to light controlled by an object to be reproduced, a photographic element bearing at least one light-sensitive silver halide emulsion layer containing an immobile dye intermediate capable of forming (1) a dye selected from the group consisting of quinoneimine- and azomethine dyes, and (2) an azo dye, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., color developing the latent image areas, forming azo dyes in the remaining areas, bleaching the color developed dye images to colorless products which remain in said layer, and removing the silver and silver salts subsequent to development.

4. A photographic color process which comprises exposing a photographic element bearing at least one light-sensitive silver halide emulsion layer containing an immobile polymeric dye intermediate capable of forming (1) a dye selected from the group consisting of quinoneimine- and azomethine dyes and (2) an azo dye, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., to light controlled by an object to be reproduced, color developing the latent image areas, forming azo dyes in the reverse areas; bleaching the color developed dye images to colorless products which remain in said layer and removing the silver and silver salts subsequent to development.

5. In a photographic color process which involves exposing a photographic element bearing at least one light-sensitive silver halide emulsion layer containing an immobile dye intermediate capable of forming (1) a dye selected from the group consisting of quinoneimine- and azomethine dyes and (2) an azo dye, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., to light controlled by an object to be reproduced, color developing the latent image areas, forming azo dyes in the reverse areas; the steps which comprise bleaching the color developed dye images to colorless products which remain in said layer and removing the silver and silver salts subsequent to development.

6. A photographic color process which comprises treating a color developed photographic element, bearing a polymeric immobile dye intermediate, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., which intermediate has been converted into dyes taken from the class consisting of azomethine and quinoneimine dyes in latent image areas, with a diazonium compound to couple the unconverted dye intermediate into azo dyes in the remaining

areas, bleaching the dyes in the latent image areas to colorless products which remain in the layer and removing the silver and silver salts from the element.

7. In a photographic color process which involves treating a color developed photographic element, bearing an immobile dye intermediate, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., which intermediate has been converted into dyes taken from the class consisting of azomethine and quinoneimine dyes in latent image areas, with a diazonium compound to couple the unconverted dye intermediate into azo dyes in the remaining areas, the steps which comprise bleaching the dyes in the latent image areas to colorless products which remain in the layer and removing the silver and silver salts from the element.

8. A process of color photography comprising exposing a photographic element bearing at least one light-sensitive silver halide emulsion layer containing an immobile dye intermediate capable of forming (1) a dye selected from the group consisting of azomethine and quinoneimine dyes and (2) azo dyes, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., developing the exposed element in an aqueous developer solution containing a primary aromatic amino developing agent, then treating said element in an aqueous solution of a diazo compound, decolorizing the dyes formed in the developing step with an acid bleach bath containing a silver oxidizing agent, and removing the silver salts subsequent to said development.

9. A process of color photography comprising exposing to a color scene a multilayer photographic element containing a plurality of differentially sensitized emulsion layers each containing an immobile color former capable of forming (1) a dye selected from the group consisting of quinoneimine- and azomethine dyes, and (2) an azo dye, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., which is complementary in color to the utilized sensitivity of the respective emulsion layers, developing the exposed element with a color developing agent, then reacting said element with a diazo compound, and decolorizing the dyes formed in said development step to colorless products which remain in the layers and removing the silver and silver salts subsequent to said development.

10. A process as set forth in claim 2 wherein a film element comprising at least two differentially sensitized emulsion layers is used.

11. A process as set forth in claim 2 wherein the color-developed dye images are decolorized prior to diazo coupling in a solution of a strong reducing agent.

12. A process as set forth in claim 2 wherein the color-developed dye images are decolorized subsequent to diazo coupling.

13. A process as set forth in claim 2 wherein decolorization of the temporary dyes and bleach-

ing of the silver images to silver salts are brought about simultaneously in an aqueous solution having a pH of between 1 and 6 and containing between 1 and 20% of an oxidizing agent capable of converting metallic silver to silver salts.

14. A process of three color photography which comprises exposing a photographic element containing three differentially sensitized silver halide emulsion layers which are so arranged and sensitized that each emulsion will record approximately one third of the visible spectrum, each layer containing an immobile dye intermediate which is capable of forming (1) a dye by color forming development and (2) an azo dye complementary in color to the utilizable sensitivity of the emulsion layer in which it is contained, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., color developing each of said layers simultaneously in the latent image areas, forming azo dyes in the reverse image areas, bleaching the color developed dyes to colorless products which remain in the film and removing the silver and silver salts subsequent to color development.

15. A process of three color photography which comprises printing from color separation records onto a photographic element containing three differentially sensitized silver halide emulsion layers which are so arranged and sensitized that each emulsion will record approximately one third of the visible spectrum, each layer containing an immobile dye intermediate which is capable of forming (1) a dye by color forming development and (2) an azo dye complementary in color to the utilizable sensitivity of the emulsion layer in which it is contained, said intermediate being a colloid containing a substituent taken from the group consisting of sulfonic and carboxylic acid radicals and water-soluble salts thereof which is further characterized by being soluble to the extent of at least 0.5% in 5% aqueous sodium carbonate at 25° C., color developing each of said layers simultaneously in the latent image areas, forming azo dyes in the reverse image areas, bleaching the color developed dyes to colorless products which remain in the film and removing the silver and silver salts subsequent to color development.

16. A process as set forth in claim 1 wherein said immobile dye intermediate contains an alkali metal sulfonate group.

17. A process as set forth in claim 9 wherein the immobile dye intermediates contain an alkali metal sulfonate group.

18. A process as set forth in claim 1 wherein said immobile dye intermediate contains an alkali metal carboxylate group.

19. A process as set forth in claim 1 wherein said dye intermediate is an amide of an ethylene-maleic anhydride polymer and 1-p-amino-phenoxyethylamino-5-naphthol.

20. A process as set forth in claim 1 wherein said color forming development is carried out with an alkaline developer solution containing an alkali metal salt of 5-amino-salicylic acid as the color coupling developing agent.

21. A process as set forth in claim 1 wherein said color forming development is carried out with an alkaline developer solution containing an alkali metal salt of 5-amino-salicylic acid as the

color coupling developing agent and said dye intermediate is an amide of an ethylene-maleic anhydride polymer and 1-p-aminophenoxyethyl-amino-5-naphthol.

22. A process as set forth in claim 1 wherein said immobile dye intermediate is a polyvinyl acetal capable of coupling with a diazo compound,

said acetal containing in addition to the coupling groups, acetal linkages from an aromatic aldehyde containing a free sulfonic acid group.

23. A process as set forth in claim 1 wherein said azo dye is formed by the use of a water solution of tetrazotized dianisidine.

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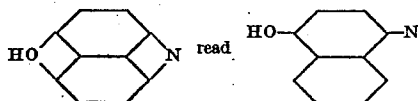
**Certificate of Correction**

Patent No. 2,297,732.

October 6, 1942.

DAVID W. WOODWARD

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, second column, lines 15-20, for that portion of the formula reading



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of November, A. D. 1942.

[SEAL]

HENRY VAN ARSDALE,  
*Acting Commissioner of Patents.*