

1

2,697,662

## COLOR CORRECTION PROCESSES

David Malcolm McQueen and Clay Weaver, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application July 24, 1951,  
Serial No. 238,384

8 Claims. (Cl. 95—2)

This invention relates to color photography. More particularly, it relates to a process of color correction utilizing an integral masking procedure. Still more particularly, it relates to a process of color correction by integral masking whereby the duplication of subtractive color reproductions is improved. The invention also relates to new photographic elements which can be processed readily to form integral color correcting masks.

The quinoneimine and azomethine dyes used in subtractive three-color photography do not possess ideal spectral absorption characteristics, this defect being particularly marked with the cyan and magenta dyes. Only the yellow dyes, as a rule, are satisfactory in that the amount of green and red light absorption is usually negligible, although sometimes a small amount of green light is absorbed. The magenta dyes usually absorb a considerable amount of blue light and a small amount of red light, both of which they should transmit. The cyan dyes usually absorb significant amounts of both blue and green light which they should transmit. When a multi-color print is made by exposure through a multi-color negative composed of these nonideal dyes, portions of all three records are introduced into each positive image because of the undesirable absorptions. For example, the magenta dye should absorb and modulate only the green printing light which records an image in the green-sensitive layer of the multilayer positive or print film. However, it also absorbs and modulates blue light to a considerable extent, and when the blue record is made (with blue printing light), the concentration of dyes in the image recorded in the blue-sensitive layer of the positive film is decreased. Undesirable blue and green absorption by the cyan dye detracts similarly from the blue and green records. This leads to desaturation of the image dyes in the respective layers and produces colors in the positive picture which are dirty or degraded.

Obviously, it is desirable to correct for the undesirable absorptions of the negative image dyes. This can be accomplished by forming in the layer concerned a colored mask which absorbs strongly in the regions of the spectrum where the image dye has its undesirable absorption. The mask may be considered to be the negative of the color-developed image insofar as density to light undesirably absorbed by the image is concerned. It is not a negative in the strict sense, since its color is not complementary. Ideally the density of the mask should be such that all unwanted absorptions are just cancelled. That is, the density of the mask throughout the layer should vary inversely with the undesirable density of the image dye so that two regions of the spectrum are transmitted uniformly, and the third region only is modulated. This is equivalent to stating that the gamma of the mask is equal, but opposite in sign, to the gamma derived from the undesirable absorption of the image dye.

A number of masking methods have been proposed. Separate masks have been used, but it is difficult to superimpose them accurately on the color picture. This difficulty has caused the development of integral masking procedures, in which colored masks are incorporated in the sensitive emulsion layer. Problems connected with masking and the principles of integral masking are summarized in U. S. Patent 2,449,966.

A prior method of color correction by integral masking utilizes colored color-formers (azo dyes of ordinary color-formers) which are converted to subtractive dye images in exposed areas by ordinary color processing. In

2

the unexposed areas, the colored color-formers remain unchanged and function as color correcting masks. However, the use of colored substances in the light-sensitive layers of a photographic element introduces light loss on exposure, because of the filtering effect of the colored materials. Furthermore, it is difficult to find colored color-formers capable of yielding correct densities and contrast values for both the primary color component image and the masking images. Usually, mixtures of colored and uncolored color-formers must be resorted to.

An azo coupling masking process has been proposed which comprises treating a color film containing color developed dye images and residual color forming compounds with an aqueous solution of an amine salt, rinsing briefly and then treating the film with an acid solution of sodium nitrite. To obtain optimum results the sodium nitrite solution may be buffered to an appropriate pH, e. g., 4 to 6.5. Suitable amine salts are the hydrochlorides of p-chloraniline, o-toluidine, o-anisidine metanilic acid, etc. The bathing and diazotization operations may be carried out at room temperature and ice temperatures are generally not required. In place of amine hydrochlorides other water-soluble salts such as sodium naphthionate in an aqueous solution containing acetic acid and sodium acetate may be used. Either monolayer or multilayer films may be masked by such procedures by selection of the appropriate amine salts. This process, however, does not have the advantages of the process of this invention because the amine salts migrate and cause undesirable color dilution.

The above difficulties can be remedied by the integral masking process of this invention which utilizes non-diffusing colorless color-formers and non-diffusing aromatic amines in water-permeable colloid silver halide layers, a color coupling development step whereby a dye image or images are formed and an azo-coupling step whereby an azo-dye mask is formed. The color component images are formed by color coupling development of latent silver salt images in such layers and residual color-formers are converted to azo dyes which function as color correcting masks for the color-developed images. This process is especially useful in the treatment of multilayer monopak film elements containing polyvinyl acetal color-formers which serve also as binders for the light-sensitive silver halides. In a preferred aspect of the invention polyvinyl acetal color formers are the binding agents for the silver salts in the water-permeable colloid layers which also contain polyvinyl aromatic amino acetals.

The photographic elements which results from the first step of the process are novel in that each developed silver halide emulsion layer contains a silver image, quinoneimine or azomethine dye image, residual color former and a colorless, non-diffusing, primary aromatic amine.

Representative polyvinyl acetal color-formers are those disclosed in U. S. patents Jennings et al., 2,397,864, issued April 2, 1946 (cyan, magenta and yellow); Martin, 2,476,988, issued July 26, 1949 (magenta); Martin, 2,489,655, issued November 29, 1949 (cyan); and McQueen, 2,513,190, issued June 27, 1950 (yellow). On exposure followed by color development in the usual color-developing solutions containing an agent such as p-aminodiethylaniline, these color-formers are converted to dyes of the azomethine or quinoneimine type. Subsequent bleaching and fixing steps clear the film of all silver and silver salts and leave a dye image in each layer. These dye images, and particularly the cyan and magenta ones, suffer the already-mentioned deficiencies as regards undesirable absorption and require color correction. The yellow color-formers need not in general be compensated for because of their slight absorption in the green region of the spectrum.

In carrying out a preferred aspect of the invention the process for preparing corrective masks in color-film comprises treating an exposed and developed multilayer color film, at least one layer of which contains (1) polyvinyl acetal dye color component image, said dye being of the azomethine or quinoneimine classes, (2) a colorless polyvinyl acetal color-former capable of forming such a dye, and (3) a colorless, diffusion-resist-

## 3

ant primary aromatic amine, with an acidic sodium nitrite solution having a pH from 2 to 6, whereby the aromatic amine is diazotized and coupled with the residual polyvinyl acetal color-former to form an azo dye.

With regard to the foregoing statements it is to be understood that both the dye (azomethine or quinoneimine) and the color-forming groups may be present in the same molecule, i. e., as a polyvinyl acetal dye containing residual color-forming groups. The primary aromatic amine (the masking intermediate), moreover, may be present as a separate component or it may form part of the polyvinyl acetal color-former, as a copolyvinyl acetal containing both color-forming groups and primary aromatic amino groups. Both modifications are illustrated in the examples which follow.

The colorless primary aromatic amine which serves as the masking intermediate should be substantially resistant to diffusion, i. e., non-migratory or immobile and have little or no tendency to migrate from the emulsion layer in which it is placed to another layer. This property is desirable in order to avoid or minimize incorrect color values which might otherwise arise from migration into other layers. Another advantage of diffusion-resistant amines is that it is possible to use different amines in respective layers of the element. Moreover, diffusion-resistant amines minimize bleeding or leaching into the various processing baths. In practice, it has been found that aromatic amines containing an aliphatic chain of at least twelve carbons linked to the aromatic nucleus are sufficiently resistant to diffusion for the purpose of this invention. Either monomeric or polymeric amines can be used. A preferred group of polymeric amines are the polyvinyl acetals containing arylamino groups. Suitable acetals are described in Dorough et al. U. S. Patent 2,310,943 and Frolich U. S. Patent 2,320,422. These polyvinyl aromatic amino acetals as previously stated may also contain color former nuclei. The latter polyvinyl aromatic aminoaldehyde acetal compounds give more sharply defined images. The latter compounds have the further advantage of more uniform dispersion and complete compatibility with the color-formers.

The process of this invention is exemplified by the procedure as follows: an emulsion of sensitive silver halides in a colorless polyvinyl acetal color-former (preferably one which forms a cyan or magenta quinoneimine or azomethine dye) is prepared by known means and suitably compounded with a colorless, non-diffusing, diazotizable amine which is preferably polymeric. The resulting emulsion is coated on film base, exposed, color-developed, fixed and bleached to remove silver and silver salts according to known procedures. There is thus obtained by the color coupling development a dye image, e. g., a cyan or magenta dye image. The film is then immersed successively in a weakly acidic aqueous solution (pH 2 to 6) and in an aqueous sodium nitrite solution, or in an acidic aqueous sodium nitrite solution of pH 2 to 6. This causes diazotization of the amine and concomitant coupling with the residual color-former. An azo dye forms in the areas where residual or unreacted color-former is available. The amine and the color-former should, of course, be selected to give an azo dye of the proper color for masking, that is, a dye whose absorption is at or near the wave length of undesirable absorption of the azomethine or quinoneimine dye. Depending upon the correction desired, the azo dye formed with a cyan color-former should be red, orange, or yellow; that formed with a magenta color-former should be yellow or green; and that formed with a yellow color-former (if any color correction is desired in the yellow layer) should be magenta or blue. The density of the corrective azo dye will be highest in the areas containing the least amount or density of azomethine or quinoneimine dye, so that the sum of the densities measured in the region of undesirable absorption will be approximately uniform throughout the film layer.

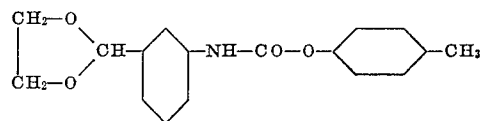
For the purpose of illustrating the invention, there are described below procedures for preparing representative non-diffusing amines, both polymeric and monomeric, which upon diazotization couple with the residual polyvinyl acetal color-former to form an azo dye corrective mask. Parts are by weight throughout.

## 4

## PROCEDURE A

*Polyvinyl acetal of m-aminobenzaldehyde*

3-(carbo-p-cresoxyamino)benzaldehyde ethylene glycol acetal,



is prepared as follows: a solution of 82.5 parts of m-aminobenzaldehyde ethylene glycol acetal (prepared as described in Example I of McQueen and Woodward, U. S. Patent 2,481,434 issued September 6, 1949) in 400 parts of acetone is mixed with a solution of 27 parts of sodium carbonate in 500 parts of water and stirred at 10–15° C. while adding 85 parts of p-cresyl chloroformate. The reaction mixture is stirred at about 25° C. for one hour, then diluted with about 500 parts of water containing about 100 parts of ice, and stirring is continued until the reaction product solidifies. The product is separated by filtration, washed with water, and recrystallized from alcohol or benzene. The yield of pure 3-(carbo-p-cresoxyamino)benzaldehyde ethylene glycol acetal, M. P. 101–102° C., is about 91 parts.

Using the general procedure of Martin U. S. Patent 2,513,189, issued June 27, 1950, the polyvinyl acetal of 3-(carbo-p-cresoxyamino)benzaldehyde, containing methylidenepheryl-o-sulfonate groups for increased solubility, is prepared as follows: a mixture of 30 parts of polyvinyl alcohol (the completely hydrolyzed material having a 4% aqueous solution viscosity of 18–24 centipoises at 20° C.) and 1 part of benzaldehyde-o-sulfonic acid, sodium salt in 180 parts of ethylene glycol is treated with 2 parts of phosphoric acid and stirred at 65° C. for 15 minutes. A solution of 6.72 parts of 3-(carbo-p-cresoxyamino)benzaldehyde ethylene glycol acetal in 15 parts of dioxane is then added slowly to the reaction mixture while stirring at 50° C. Following addition, the mixture is stirred for one hour at 65–75° C., cooled to 25–30° C., then treated with 10–20 parts of a 20% solution of triethylamine in methanol to neutralize the phosphoric acid. About 150–200 parts of acetone is then added and the precipitated polymer is filtered and thoroughly washed with acetone, methanol and again acetone. There is obtained 36 parts of the polyvinyl acetal of 3-(carbo-p-cresoxyamino)benzaldehyde containing methylidenepheryl-o-sulfonic acid, sodium salt groups.

Finally, the protective carbo-p-cresoxy group is eliminated as follows: a solution of 11 parts of the above polyvinyl acetal in 200 parts of ethanol and 300 parts of water is treated with four parts of a 10% aqueous solution of sodium hydroxide. The alkaline mixture is stirred at 60–70° C. for 10 minutes, cooled to about 25° C. and neutralized with dilute acetic acid. The free polymeric amine resulting from the hydrolysis of the protective group is precipitated by addition of excess acetone, washed with ethanol and dried. There is obtained about 10 parts of a polyvinyl acetal of m-aminobenzaldehyde which also contains methylidenepheryl-o-sulfonic acid, sodium salt groups.

This compound (i. e., the polyvinyl acetal of m-aminobenzaldehyde, containing sodium methylidenepheryl-o-sulfonate) can also be prepared in a more direct manner as follows: a mixture of 33 parts of polyvinyl alcohol and 150 parts of ethylene glycol is treated with a solution of 2.5 parts of benzaldehyde-o-sulfonic acid sodium salt in 50 parts of ethylene glycol and 2.5 parts of phosphoric acid fortified with phosphoric anhydride and stirred at 65–70° C. for 30 minutes. A solution of 7.5 parts of m-aminobenzaldehyde ethylene glycol acetal (Example I of McQueen and Woodward U. S. Patent 2,481,434, issued September 6, 1949) in 25 parts of ethylene glycol is added and stirring is continued for 30 minutes. The product is isolated as described above for the polyvinyl acetal of 3-(carbo-p-cresoxyamino)benzaldehyde. There is obtained 38 parts of a light tan colored polyvinyl mixed acetal of m-aminobenzaldehyde and sodium benzaldehyde-o-sulfonic acid.

## PROCEDURE B

*Polyvinyl acetal of 3-amino-4-methoxybenzaldehyde*

3-(carbo-p-cresoxyamino)-4-methoxybenzaldehyde ethylene glycol acetal is prepared by the procedure of Pro-

cedure A, using 97.5 parts of 3-amino-4-methoxybenzaldehyde ethylene glycol acetal (see Example IV of McQueen and Woodward U. S. Patent 2,481,434, issued September 6, 1949). The compound melts at 133–134° C.

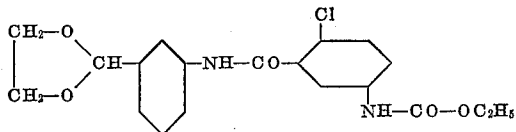
The corresponding polyvinyl acetal is prepared as in Procedure A, using 7.5 parts of 3-(carbo-p-cresoxy-amino)-4-methoxybenzaldehyde ethylene glycol acetal and 3 parts of benzaldehyde-o-sulfonic acid, sodium salt. Finally, hydrolysis of the protective carbo-p-cresoxy group is carried out as in Procedure A, yielding the polyvinyl mixed acetal of 3-amino-4-methoxybenzaldehyde and benzaldehyde-o-sulfonic acid, sodium salt.

This polyvinyl mixed acetal compound can also be prepared more directly by means of the procedure described in the last paragraph of Procedure A, replacing the m-aminobenzaldehyde ethylene glycol acetal of Procedure A with 9 parts of 3-amino-4-methoxybenzaldehyde ethylene glycol acetal (Example IV of McQueen and Woodward U. S. Patent 2,481,434, issued September 6, 1949).

#### PROCEDURE C

##### *Polyvinyl acetal of m-(5-amino-2-chlorobenzamido)-benzaldehyde*

The ethylene glycol acetal of m-(5-carbomethoxyamino-2-chlorobenzamido)benzaldehyde,



is prepared as follows: a solution of 86 parts of 2-chloro-5-aminobenzoic acid in 500 parts of water containing 106 parts of sodium carbonate is stirred at 40° C. while adding 55 parts of ethyl chloroformate. After the heat of the reaction has subsided, the mixture is stirred at 80° C. for 30 minutes, then diluted with 500 parts of water and ice. The product is precipitated by adding concentrated hydrochloric acid and filtered. The crude 5-carbomethoxyamino-2-chlorobenzamido acid is purified by crystallization from ethanol, giving 74 parts of material melting at 177–178° C. This is converted to the acid chloride by treatment of 50 parts of it with thionyl chloride. A solution of the acid chloride thus obtained in 75 parts of dioxane is added slowly with stirring at 20–25° C. to a mixture of 33 parts of m-aminobenzaldehyde ethylene glycol acetal in 200 parts of dioxane and 42 parts of sodium carbonate in 125 parts of water. The reaction mixture is stirred for about 4 hours at 20–25° C. On addition of water, the solid reaction product precipitates and is filtered and crystallized from ethanol. There is obtained 51 parts of pure m-(5-carbomethoxyamino-2-chlorobenzamido)benzaldehyde ethylene glycol acetal, M. P. 144–145° C.

The corresponding polyvinyl acetal, containing methylenediphenyl-o-sulfonic acid groups for increased solubility, is prepared as follows: a mixture of 50 parts of polyvinyl alcohol with 250 parts of ethylene glycol is treated with a solution of 2 parts of benzaldehyde-o-sulfonic acid sodium salt in 50 parts of ethylene glycol and 3.5 parts of phosphoric acid fortified with phosphoric anhydride. The mixture is stirred at 65–70° C. for 30 minutes, then treated with a solution of 8 parts of m-(5-carbomethoxyamino-2-chlorobenzamido)benzaldehyde ethylene glycol acetal in 50 parts of ethylene glycol and 40 parts of acetone. After stirring at 65–70° C. for one hour, the polyvinyl acetal is isolated as in Procedure A. The hydrolysis of the carbomethoxy protective group is carried out as in Procedure A except that the alkaline treatment requires 2–3 hours for best results. There is thus obtained the polyvinyl mixed acetal of m-(5-amino-2-chlorobenzamido)benzaldehyde and benzaldehyde-o-sulfonic acid, sodium salt.

The same polyvinyl acetal can also be prepared using as the starting material m-(5-carbomethoxyamino-2-chlorobenzamido)benzaldehyde ethylene glycol acetal or m-(5-carbo-p-cresoxyamino-2-chlorobenzamido)benzaldehyde ethylene glycol acetal. These products are prepared by replacing the ethyl chloroformate in the first paragraph of Procedure C with an equivalent quantity of methyl chloroformate or p-cresyl chloroformate, respectively.

#### PROCEDURE D

##### *2-amino-5-dodecylbenzenesulfonic acid*

This compound is prepared as described in British Patent 469,108.

#### PROCEDURE E

##### *3-amino-5-stearamidobenzoic acid*

A mixture of 30 parts of 3-nitro-5-aminobenzoic acid (Hubner, Ann. 222, 81, (1884)), 50 parts of stearoyl chloride and 100 parts of pyridine is heated for three hours at 90–100° C. The pyridine is then removed under reduced pressure and the residue is stirred with dilute hydrochloric acid, filtered and washed with water. Crystallization from methanol yields 58 parts of 3-nitro-5-stearamidobenzoic acid, M. P. 148–153° C. A mixture of 50 parts of 3-nitro-5-stearamidobenzoic acid, 150 parts of ethanol and 2 parts of palladium-on-charcoal catalyst is charged into an oscillating autoclave and hydrogenated at 75° C. and at a pressure of 1500 lbs./sq. in. The reaction product is separated by filtration from the chilled solution, dissolved in 100 parts of dioxane and this solution is filtered to remove the catalyst. Crystallization from a dioxane-alcohol mixture yields 34 parts of 3-amino-5-stearamidobenzoic acid, M. P. 184–187° C.

The photographic color masking methods and novel photographic elements of this invention are further illustrated by the following examples. The parts stated are parts by weight.

#### EXAMPLE I

A photographic silver halide emulsion is prepared by adding a solution consisting of 29 parts of 3N silver nitrate and 29 parts of 20% ammonium hydroxide to a mixture consisting of 100 parts of a 5% solution in 20% aqueous alcohol of the magenta color-forming polyvinyl acetal of Example I of U. S. Patent 2,476,988 (i. e., m-[p-(5-ethylcarbonato-3-methyl-1-pyrazolyl)benzamido]benzaldehyde polyvinyl acetal), 30 parts of water, 25 parts of ethanol, 31 parts of 3 N ammonium bromide and 2 parts of 0.5 N potassium iodide. The dispersion is stirred for 30 minutes, coagulated with an excess of 15% aqueous sodium sulfate, and the coagulum is washed in running water. One hundred (100) parts of a 5% aqueous alcoholic solution of the same magenta color-former is mixed with the coagulum, the total weight is adjusted to 200 parts with 20% ethanol and the emulsion is stirred at 60–70° C. until homogeneous. To this emulsion is added 80 parts of a 5% solution of the 3-amino-4-methoxybenzaldehyde polyvinyl acetal of Procedure B in 20% aqueous alcohol. The resulting emulsion is then treated with the usual coating aids and sensitizers, its viscosity is suitably adjusted with 20% alcohol, and it is coated on a transparent film base as described in U. S. Patent 2,534,326. The dried photographic element is exposed and processed to a magenta image by developing in a solution composed of the following ingredients:

|                                     | Parts |
|-------------------------------------|-------|
| p-Aminodiethylaniline hydrochloride | 2     |
| Sodium sulfite (anhydrous)          | 10    |
| Sodium carbonate monohydrate        | 20    |
| Sodium bromide                      | 2     |
| Water                               | 1000  |

The element is then rinsed, fixed in a 20% solution of sodium thiosulfate, washed, bleached in a 4% solution of potassium ferricyanide, again washed, fixed in a 25% solution of sodium thiosulfate and washed. The film, which now bears a magenta image, is bathed for two minutes in a 0.25 molar solution of potassium acid phthalate (pH 4.0), rinsed and then bathed for two minutes in a 2.5% solution of sodium nitrite, whereby diazotization of the amine and coupling with the residual color-former takes place. A yellow dye forms in the areas where residual or unreacted magenta color-former is available. The density of the yellow dye is highest in areas of the film containing the least magenta dye, so that the sum of the densities to blue light of the magenta and yellow dyes is approximately uniform throughout the film.

An alternative process is to color-develop, rinse, fix and wash as described in the first four steps above, then mask by bathing the film in a mixture of buffer and sodium nitrite or an acidic solution of sodium nitrite. The film is then washed, bleached, fixed and again washed to give

the finished masked image. This alternative procedure results in a clearer finished image.

When instead of 80 parts of the 5% aqueous alcoholic solution of 3-amino-4-methoxybenzaldehyde polyvinyl acetal, there is used only 60 parts of the same solution, there is obtained a magenta image with a lighter colored yellow mask. In this way one can control the image to mask ratio with respect to density and gamma.

#### EXAMPLE II

The procedure of Example I is repeated in all details except that the polyvinyl acetal of 3-amino-4-methoxybenzaldehyde is replaced by 60 parts of a 5% solution in 20% ethanol of the polyvinyl mixed acetal of m-aminobenzaldehyde and benzaldehyde-o-sulfonic acid sodium salt, prepared as described in Procedure A. There was obtained a masked magenta image similar to that of Example I.

Similar results are obtained by using, as the masking intermediate, 80 parts of a 5% solution in 20% aqueous alcohol of m-(5-amino-2-chlorobenzamido)-benzaldehyde-sodium benzaldehyde-o-sulfonate polyvinyl acetal, prepared as in Procedure C.

#### EXAMPLE III

A photographic emulsion is made as in Example I by using in place of the magenta color-former a mixture of equal parts of two cyan color-formers, these being the polyvinyl acetal of m-(1-naphthol-2-sulfonamido)benzaldehyde (Woodward U. S. Patent 2,423,572, issued July 8, 1947) and the polyvinyl acetal of m-(3-methylsalicylamido)benzaldehyde (Martin U. S. Patent 2,538,257, issued January 16, 1951) which acetals may be simple or mixed, e. g., modified by methylidene-phenyl sulfonate groups as taught in said patents. To the silver halide emulsion is added 80 parts of a 5% solution in 20% aqueous alcohol of 3-amino-4-methoxybenzaldehyde polyvinyl acetal. The emulsion is coated and processed as in Example I to give a cyan image containing a pinkish-orange dye mask throughout the picture in amounts dependent upon the available color-former. The blue and green absorption throughout the layer is substantially uniform.

Similar results are obtained using m-aminobenzaldehyde polyvinyl acetal as the masking intermediate. If a lower density of masking dye is desired, a smaller amount of masking intermediate is used.

#### EXAMPLE IV

A multilayer photographic element is made by coating as the first layer on a transparent support the magenta color-forming silver halide emulsion of Example I, containing 80 parts of a 5% solution of 3-amino-4-methoxybenzaldehyde polyvinyl acetal as the masking intermediate, and a sensitizing dye which confers green sensitivity; then coating a separator layer from a 2.5% solution in 20% ethanol of the hydrolyzed ethylene/vinyl acetate copolymer described in McQueen U. S. Patent 2,397,866, April 2, 1946; then coating as the second color-forming layer the cyan color-forming silver halide emulsion of Example III, containing 60 parts of a 5% solution of 3-amino-4-methoxybenzaldehyde polyvinyl acetal and a sensitizing dye which confers red sensitivity, then coating a separator layer identical with the one previously used; and finally coating a yellow color-forming silver halide emulsion, prepared as described in Example I of Martin U. S. Patent 2,513,189, June 27, 1950, and containing a soluble yellow dye such as the one having Colour Index No. 640. When the finished element is exposed with blue, green, and red light, respectively, a yellow, magenta, and cyan image results. The exposed film is processed and treated with an aqueous solution of sodium nitrite and an acidic buffer as in Example I. This treatment develops the masking dye by coupling with the available color-former in the cyan and magenta layers. There results a three-color image having colored masks integral with the cyan and magenta layers.

#### EXAMPLE V

To 75 parts of a magenta color-forming silver halide emulsion prepared as described in Martin U. S. Patent 2,513,189, issued June 27, 1950, is added 10 parts of a 10% solution of 2-amino-5-dodecylbenzenesulfonic acid (Procedure D). The emulsion is coated on a transparent film base, exposed and processed as in Example I to give a magenta image which has a yellow mask.

#### EXAMPLE VI

To 100 parts of a magenta color-forming emulsion prepared as described in Martin U. S. Patent 2,513,189, issued June 27, 1950, is added 0.4 part of 3-amino-5-stearamidobenzoic acid (Procedure E) as the ammonium salt. The emulsion is coated on a film base, exposed and processed as in Example I to give a magenta image. The film is then immersed in an acetic acid-sodium acetate buffer solution having a pH of 4, then in 2% aqueous sodium nitrite, and washed. This treatment forms a yellow azo dye mask in the film.

A cyan color-forming emulsion such as that of Example III when treated in a similar manner gives a cyan image which has an orange mask.

#### EXAMPLE VII

This example illustrates the use of a compound wherein the polyvinyl acetal color-former and the diazotizable amine are present in the same molecule, rather than as two separate compounds, and therefore the azomethine or quinoneimine dye and the azo dye are parts of the same molecule in the finished film. In other words, this example uses a single polyvinyl acetal which combines the functions of silver halide binder, subtractive color-former and masking intermediate.

A mixture of 33 parts of polyvinyl alcohol in 100 parts of ethylene glycol is treated with a mixture of 1 part of m-aminobenzaldehyde ethylene glycol acetal and 5 parts of 3-[4-(5-ethylcarbonato-3-methyl-1-pyrazolyl)benzamido]benzaldehyde ethylene glycol acetal (Martin U. S. Patent 2,476,987, issued July 26, 1949) in 75 parts of ethylene glycol, then with 1 part of benzaldehyde-o-sulfonic acid sodium salt dissolved in 25 parts of 85% phosphoric acid. The mixture is stirred at 65-70° C. for 45 minutes, cooled and treated with 200 parts of acetone and filtered. The product is washed and dried as in Procedure A. There is obtained 38 parts of a polymer which is a polyvinyl mixed acetal containing units of a magenta color-former and of a diazotizable amine, besides sodium methylidenephényl sulfonate groups.

A solution is made containing 5 parts of the above polyvinyl mixed acetal in 15 parts of ethanol and 80 parts of water, and coated on film base. When the dried coating is treated with a p-phenylenediamine color developer followed by a bleaching agent such as 4% potassium ferricyanide, a magenta color results. When a sample of the film is bathed in a solution of sodium nitrite, followed by bathing in a solution of potassium acid phthalate (pH 4), or of any weak acid having a pH of less than 6, e. g., acetic acid, a yellow color results. Alternatively, a mixture of sodium nitrite solution and acidic solution can be used.

The mixed polyvinyl acetal compound described above is tested in a photographic element as follows: a silver halide emulsion is made by the general procedure of Martin U. S. Patent 2,513,189, issued June 27, 1950 using the polyvinyl mixed acetal as the halide binder. The emulsion is coated on a photographic support, exposed and processed to a magenta image. It is then treated with sodium nitrite and an acidic buffer as above, thereby causing diazotization of the amine and coupling with the residual color-former. The finished picture contains a yellow masking dye of greatest density in the areas where the magenta dye has the least density.

#### EXAMPLE VIII

This example illustrates the use in the emulsion layer of a diazotizable amine, in this case a polyvinyl acetal containing primary aromatic amino groups, in which the amino groups are protected by a hydrolyzable group until just prior to diazotization. Protected amines of this type have the advantage of greater stability than free amines. They are characterized moreover by freedom from side reactions and of possible injurious effect on the silver halide emulsion during aging.

A photographic emulsion is made as in Example I, but using a mixture of equal parts of the two cyan color-formers described in Example III. To the silver halide emulsion is added 80 parts of a 2.5% solution in 20% aqueous ethanol of the polyvinyl acetal of 3-(carbo-p-cresoxyamino)-4-methoxybenzaldehyde, containing sodium methylidenephényl-o-sulfonate groups, described in Procedure B. In this compound, the diazotizable amino groups are protected by carbocresoxy groups. The emulsion is coated on a film base and color developed as in

Example I to give a cyan image. The color-developed film is then bathed for five minutes in 2% aqueous sodium hydroxide at room temperature. This treatment hydrolyzes the protective groups. After washing in water, the film is treated with a sodium nitrite solution as in Example I. There is then obtained a masked cyan image similar to that of Example III.

It should be noted that when using protected amines as just described, it is unnecessary in some cases to go through a separate hydrolysis step. When the protective group is readily hydrolyzable, it may be removed during color development or during color fixing, thus avoiding an additional alkaline treatment. More resistant protective groups can be removed as described, using dilute alkaline solutions, e. g., 0.1%–2% sodium hydroxide or potassium hydroxide solutions.

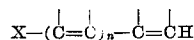
In the process of this invention there may be used any colorless primary aromatic amine containing an aliphatic radical having a chain length, exclusive of the aromatic nucleus, of at least twelve aliphatic carbons. By "primary aromatic amine" is meant, of course, a compound having a primary amino group directly attached to aromatic nucleus, e. g., benzene or naphthalene or to a heterocyclic nucleus having aromatic properties, e. g., pyridine, quinoline, benzothiazole, antipyrine (1-phenyl-2,3-dimethylpyrazolone-5) etc. For convenience in preparing and coating the light-sensitive emulsions, the amine should be desirably soluble or dispersible in water or water-ethanol mixtures containing up to 95% ethanol. In addition to the amines employed in the foregoing examples, other suitable amines include such monomeric primary aromatic amines as 2-tetradecoxylaniline, 2-octadecoxylaniline, 4-octadecoxylaniline, 2-octadecoxylaniline-5-sulfonic acid, 4-tetradecoxylaniline-3-sulfonic acid, 4-aminolauranilide, 5-stearamido or thanilic acid, 5-octadecanesulfonamido or thanilic acid, 3-amino-N-dodecylbenzamide, 4-amino-2-methyl tetradecanesulfonamido, N'-dodecylsulfanilamide, and the like.

As previously stated, polymeric aromatic amines are preferred, i. e., amines having a molecular weight in excess of about 1000 and containing a large number of recurring units in substantially linear arrangement, said units containing primary arylamino groups. In particular, polyvinyl acetals containing primary arylamino groups are preferred because of their superior compatibility with the polyvinyl acetal color-formers. Example of polymeric amines include the aminostyrene/maleic acid copolymers, the aminostyrene/acrylic acid copolymers, the styrene/m-aminophenylmaleamic acid copolymers, the polymers of 3-acrylamido-5-aminobenzoic acid, and the like. Several examples of the preferred materials, that is, the polyvinyl acetals containing primary arylamino groups are described in the foregoing procedures, examples and patents. To these may be added, for example, the polyvinyl acetal of 3-amino-5-chlorobenzaldehyde; the polyvinyl acetal of 3-amino-1-, naphthaldehyde; and the numerous aminobenzaldehyde polyvinyl acetals which are obtained by acetal interchange with polyvinyl alcohol of the substituted aminobenzaldehyde acetals of McQueen and Woodward U. S. Patent 2,481,434, September 6, 1949. As illustrated above, the color-former groups and the amine groups may be present in the same polymer molecule. As already mentioned, a preferred embodiment is that where the primary aromatic amine group is protected by a hydrolyzable group.

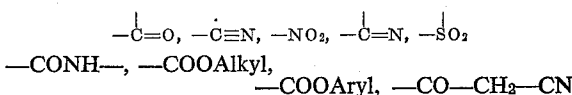
There may be employed any polyvinyl acetal color-former convertible by color development to a dye of the azomethine or quinoneimine class and capable of coupling with a diazonium compound. A number of such color-formers have been described in the prior art relating to color photography. These polyvinyl acetal color-formers, which serve also as the binding agents for the silver halides, may if desired, contain water-solubilizing groups to increase their water-sensitivity. For example, the carboxyl or sulfonic acid groups can be introduced by partial acetalization of the polyvinyl alcohol with phthalaldehydic acid or o-sulfobenzaldehyde or their alkali metal salts as taught above.

While polyvinyl acetal color formers have been described in the foregoing examples, the invention is not limited to such preferred color formers. To the contrary, in the broader aspects of the invention any non-diffusing color-former can be used. A large number of suitable nondiffusing color formers are known to the art and they vary widely in chemical structure and consti-

tution. These color formers, however, all contain a nucleus possessing a structure of the formula



where X is a member taken from the group consisting of hydroxyl and primary and secondary amine radicals and n is 0 or 1. The color-forming nucleus thus may be a phenol or naphthol having a coupling position available ortho or para to the aromatic hydroxyl group or an active methylene compound; that is, a compound containing a  $-CH_2-$  group activated by conjugated groups taken from the class



connected directly or through a conjugated system. Such active methylene compounds or nuclei are distinguished by their ability to have one of the hydrogen atoms of the methylene groups replaced by alkali metal in an aqueous solution and includes many cyclic and heterocyclic compounds which are described in the literature. Suitable materials are the cyan and magenta color-formers of U. S. Patents 2,179,234, 2,179,238, and 2,179,239.

Other suitable binders besides the preferred polyvinyl acetals are gelatin, polyvinyl alcohol, the water-soluble polyamides, albumin, agar-agar, casein, water-soluble cellulose derivatives, hydrolyzed mono-olefin/vinyl ester copolymers, etc.

The diazotization and coupling steps are preferably carried out by first immersing the film, plate or paper bearing the dye image in an aqueous solution having a pH between 2 and 6 for a time sufficient to afford complete impregnation, e. g., 1 to 10 minutes. Suitable acidic solutions are those containing dilute acids such as hydrochloric, sulfuric, acetic acid and the like, or buffer solutions of the proper pH such as potassium chloride-hydrochloric acid, sodium dihydrogen phosphate, sodium citrate, sodium acetate, potassium acid phthalate, sodium hydrogen sulfate and the like. The film is then rinsed if desired and immersed in an aqueous sodium nitrite solution of 0.1–10%, preferably 1–5% concentration again for 1 to 10 minutes. These two operations can, however, be simultaneous in that the film is immersed in an acidified sodium nitrite solution for the specified time. It is not necessary in these steps, particularly when they are separate, to operate at low temperature, although there is, of course, no desirable purpose in exceeding a temperature of 25–30° C. A satisfactory temperature range is 5–20° C.

As already noted, bleaching of the residual silver can be carried out after the diazotization and coupling step rather than prior to it, if desired. This alternative procedure has been found to give extremely bright colored masks and permits the use of smaller quantities of aromatic primary amino compounds to produce adequate masking.

To accomplish efficient masking without adding excessive background density to the negative, it is desirable to form little or no masking dye in areas of the negative where image dye density is high. Rather it is preferred to adjust upward the degree of absorption in relatively less dense areas by forming mask dyes in those areas to produce a uniform absorption approximating the unwanted absorption in the high image density areas. As has been described, this is accomplished by forming azo dyes from amino components of the layer and the uncoupled color-former, remaining in the layer after color development of the dye image, these azo dyes having the desired color for masking purposes. Since the concentration of uncoupled color-former will be greatest in areas of lowest image density, maximum concentration of azo dyes will form and produce highest mask density as desired, while in areas of highest image density, most of the color-former will have been utilized in color development, and the resulting low color-former concentration will produce the desired low mask density.

In order to realize adequate control of mask density, it is necessary to establish the proper color-former/amine ratio in the layer. The color-former must be present in sufficient quantity to produce the desired image density, but a large excess of color-former is to be avoided in order to keep background density at a minimum. The amount of amine used in relation to the color-former

is dictated by the density of the mask required and will vary depending upon the particular compounds used, as well as upon density requirements. In addition, the amount of color-former and amine employed will vary in different types of emulsions depending upon the speed and gamma requirements. Thus, it is not possible to set down exact limits for the ratio of aromatic primary amine to color-former. However, it can be said as a general rule that approximately from 0.05 to 0.75 mole of amine per mole of color-former will be satisfactory, and in most cases from 0.15 to 0.55 mole of amine is used per mole of color-former. With polymeric compounds, the term "mole" refers, of course, to the molecular weight of the repeating unit.

Additional control over masked density is possible through the use of a mixture of two or more color-formers which give strong image dyes of the same color upon color development, but only one of which gives a strong azo dye mask.

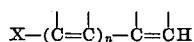
It will be apparent from the foregoing discussion that the essential principle of this invention is that the azo dyes formed in situ by diazotization and coupling are not the image dyes. They function merely as the color correcting masks for the azomethine and quinoneimine image dyes which are formed by the color coupling development of latent silver halide images.

Multilayer monopak films which contain the integral masks described above, particularly in the magenta and cyan layers, can be used in several ways. For example, they may be used as a color negative camera film for original recording. Their principal use, however, is as color duplicating negatives serving as an intermediate step in reproducing from a positive (reversal) monopak original or from primary analysis black and white separation positive records. Thus, self-masking color duplicate negatives made according to this invention can be used to print multiple copies of color-corrected positive prints.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A process for making a color component image record with an integral mask which comprises developing a film element bearing an exposed light-sensitive silver halide layer containing a colorless polyvinyl acetal color-former which contains a nucleus possessing a structure of the formula



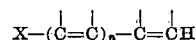
where X is a member of the group consisting of hydroxyl and primary and secondary amine radicals and  $n$  is a number taken from the group consisting of 0 and 1, said layer also containing a non-diffusing colorless high molecular weight aromatic amine containing an aliphatic chain of at least 12 carbon atoms, in an aqueous solution containing an aromatic amino color developing agent, treating the developed film in an aqueous acidic sodium nitrite solution whereby said amine is diazotized and coupled with the residual color-former to form an azo dye image.

2. A process as set forth in claim 1 wherein said

amine is a polymeric amine having a molecular weight of at least 1000.

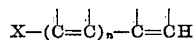
3. A process as set forth in claim 2 wherein said aromatic amine is an aromatic aminoaldehyde polyvinyl acetal.

4. A process for making a color component image with an integral mask which comprises developing a film element bearing an exposed light-sensitive silver halide dispersion in a polyvinyl acetal color-former layer, said color-former containing a nucleus possessing a structure of the formula



where X is a member of the group consisting of hydroxyl and primary and secondary amine radicals and  $n$  is a number taken from the group consisting of 0 and 1, said layer also containing a non-diffusing colorless high molecular weight aromatic amine containing an aliphatic chain of at least 12 carbon atoms, in an aqueous solution containing an aromatic amino color developing agent, treating the developed film in an aqueous acidic sodium nitrite solution whereby said amine is diazotized and coupled with the residual color-former to form an azo dye image.

5. A process for making a color correction mask in a multilayer color film which comprise developing a photographic element bearing three exposed light-sensitive silver halide layers each of which contains a different colorless polyvinyl acetal color former which contains a nucleus possessing a structure of the formula



where X is a member of the group consisting of hydroxyl and primary and secondary amine radicals and  $n$  is a number taken from the group consisting of 0 and 1, said color formers each being capable of forming a different subtractive color dye taken from the group consisting of quinoneimine and azomethine dyes, each of said layers also containing a non-diffusing colorless high molecular weight aromatic amine containing an aliphatic chain of at least 12 carbon atoms, in an aqueous solution containing an aromatic amino color-developing agent, treating the developed film in an aqueous acidic sodium nitrite solution whereby said amine is diazotized and coupled with the residual color-former to form an azo dye image.

6. A process as set forth in claim 5 wherein said amine is a polymeric amine having a molecular weight of at least 1000.

7. A process as set forth in claim 6 wherein said amine is an aromatic aminoaldehyde polyvinyl acetal.

8. A process as set forth in claim 7 wherein said aminoaldehyde is m-aminobenzaldehyde.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

| Number    | Name         | Date           |
|-----------|--------------|----------------|
| 2,306,410 | Schinzel     | Dec. 29, 1942  |
| 2,328,034 | Sease et al. | Aug. 31, 1943  |
| 2,449,966 | Hanson       | Sept. 21, 1948 |

##### FOREIGN PATENTS

| Number  | Country       | Date          |
|---------|---------------|---------------|
| 503,824 | Great Britain | Apr. 11, 1939 |