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MUTICOLOR ELEMENTS FOR COLOR PHOTOGRAPHY

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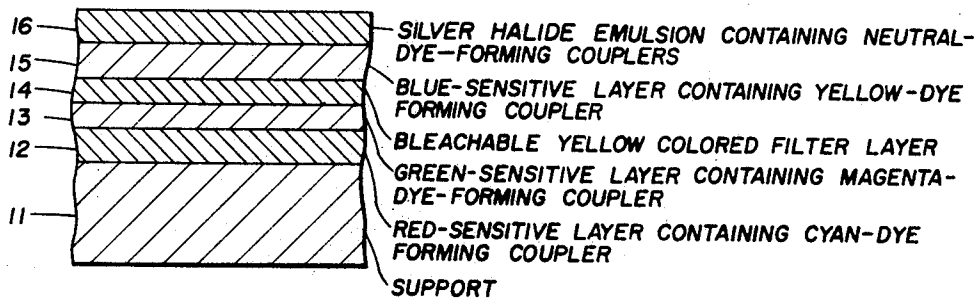

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MULTICOLOR ELEMENTS FOR COLOR PHOTOGRAPHY

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ABSTRACT OF THE DISCLOSURE

A light-sensitive photographic material comprising:

(1) A multicolor multilayer photographic color element containing incorporated color-forming couplers that form a color reproduction upon color processing, and

(2) A light-sensitive emulsion layer that forms upon color processing a silver-bleach-resistant equivalent-neutral-printing image and has a different photographic speed than the said color element is used to advantage in photography;

in one embodiment the said emulsion layer is faster than the color element and produces an image contrast that is essentially the same as the color image contrast, in another embodiment the emulsion layer is slower by an amount that is approximately equal to the useful latitude of the said multicolor element and the contrast of the said layer is higher than the contrast of the said multicolor element.

This invention relates to photography and in one of its aspects, to certain novel light-sensitive film-forming compositions used to form a special layer that is a complete image-forming unit coated together with a color photographic element on a common support and to the use of said novel elements in color photography.

In the technical applications of color photography there are many instances where it is advantageous to be able to produce a monochrome or a neutral rendition of an original scene, a portion of an original scene, or in some cases, an entirely separate scene, along with the normal full-color rendition. Thus, the much higher sensitivities available in black-and-white panchromatic films than in color materials of comparable graininess and acutance, permit photographing on a separate black-and-while element details that could not be recorded in the slower color element. Similarly, where full-color, continuous-tone material, such as a portrait, and lettering or other line copy are to be combined, the color reproduction and the black-and-while reproduction can be prepared conveniently by means of a sensitive material comprising separate sensitive elements tailored to the specific requirements of the subject matter. Where neutral-printing masks are desired, it is convenient and obviates registration problems if the mask can be prepared in a separate sensitive element integral with the color negative material.

Most of these requirements could be satisfied by the use of a suitably sensitized silver halide layer which could be developed to a silver image in the course of processing the color negative material. However, in processing conventional incorporated-coupler multicolor negative materials to subtractive dye images, the negative silver image and the residual silver halide are removed by the use of bleaching and fixing baths which would destroy and remove the silver in such a separate neutral silver image-forming layer. As a consequence, no multicolor negative material has been made available which would enable simultaneous production of a separate neutral-printing image in the course of normal color processing.

We have found a way to satisfy this need with a material which enables simultaneous preparation of a normal three-color negative and of a neutral-printing image of all or part of the same scene or of a separate scene.

It is an object of this invention to provide a novel incorporated-coupler multicolor negative material containing, as a special layer, a photographic emulsion which will provide, without additional processing, substantially neutral-printing images.

It is a further object of this invention to provide such novel material in which the special layer forms, without additional processing, a substantially neutral masking image.

It is an object of our invention to provide a novel light-sensitive multilayer negative material capable of producing a multicolor reproduction in one exposure range, a panchromatic black-and-white reproduction in another exposure range, and a photographically acceptable picture combining black-and-white type and multicolor type reproduction in the intervening exposure range.

It is another object to provide a novel multicolor photographic negative material incorporating a layer which automatically reproduces an equivalent-neutral-density highlight mask without additional exposure or processing.

It is another object of our invention to provide a film-forming light-sensitive composition containing at least one photographic silver halide emulsion and an incorporated essentially neutral-density-forming coupler composition, said light-sensitive composition producing upon exposure and color photographic processing a silver-bleach-resistant equivalent-neutral-printing image.

Still another object is to provide a process for exposing our novel element to a light image, color developing, bleaching and fixing to simultaneously produce a color image reproduction in the three selectively color sensitized layers and an equivalent-neutral-printing image in our special novel layer that is in itself a complete image-forming unit.

Still other objects will become apparent from the following specification and claims.

These and other objects are accomplished according to our invention by providing a novel light-sensitive film forming composition that is used to advantage in forming a special layer that is a complete image-forming unit in association with a multicolor element on the same support. Our special layer on latent image exposure, yields, in the course of normal negative color processing (including color development, silver bleaching and fixing), an equivalent-neutral-printing image. By an equivalent-neutral-printing image we mean an image which will produce a visual neutral when printed on a conventional color print material. Our substantially neutral-image-forming layer is advantageously coated over the outermost color-image-forming layer of a multilayer, multicolor negative photographic element. However, this layer may also be positioned elsewhere in the multilayer element, e.g., as an undercoat. It will be apparent that a normal silver image formed from a conventional panchromatic silver halide emulsion cannot be used because it will not withstand the silver bleach treatment in the negative color process.

The special layers of our invention produce a silver-bleach-resistant equivalent-neutral-printing image. Our invention is not limited by the specific compositions of these layers. The special layer is advantageously panchromatically sensitized, that is, sensitive to blue, green, and red light. However, layers with orthochromatic response, that is, sensitive under normal exposing conditions to blue and green light, can be used. Layers sensitive under normal exposing conditions to red and green or blue can also be used.

One advantageous form of the invention uses one or

a mixture of couplers in the special layer to produce the desired neutral-printing image in the form of one dye or a mixture of dyes.

Another useful form of our special layer uses a coupler, such as p-benzylphenol, which, in the dye-forming reaction, yields a dye which protects the associated developed silver from the action of the bleach.

The bleach-resistant black-and-white equivalent-neutral-image-producing layers advantageously contain any of the camera speed silver halide emulsions, preferably silver bromoiodide dispersed in one or a mixture of the hydrophilic colloids useful in photographic emulsions which include such naturally occurring materials as gelatin, albumin, agar-agar, gum arabic, alginic acid, and such synthetic hydrophilic resins as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ether, partially hydrolyzed cellulose acetate, etc. The silver halide may be blue and red sensitive or orthochromatically sensitized, but will ordinarily be panchromatically sensitized, which can be done with well known optical sensitizing dyes, e.g., the cyanine and merocyanine dyes, such as those described in U.S. Patents 1,846,301; 1,846,302; 1,942,854; 2,112,140; 2,165,338; 2,493,747; 2,739,964; 2,493,743; 2,503,776; 2,519,001; 2,666,761; 2,734,900; 2,739,149; and British Patent 450,958.

The emulsions used in preparing the photographic elements of the invention can be chemically sensitized by well known procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added, such as those described in U.S. Patents 1,574,944; 1,623,499; and 2,410,689. The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which can be used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in U.S. Patent 2,448,060, and as antifoggants in higher amounts as described in U.S. Patents 2,566,245 and 2,566,263. The emulsions can contain gold salts in sensitizing amounts as described in U.S. Patent 2,399,083, or in stabilizing amounts as described in U.S. Patents 2,597,856, and 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloric, and 2-aurosulfobenzothiazole methochloride. The emulsions can contain sensitizing amounts of reducing agents such as stannous salts (U.S. Patent 2,487,850), polyamines, such as diethylene triamine (U.S. Patent 2,518,698), polyamines, such as spermine (U.S. Patent 2,251,925), or bis (β-aminoethyl)-sulfide and its water-soluble salts (U.S. Patent 2,521,926).

The emulsions can contain speed-increasing compounds of the quaternary ammonium type of U.S. Patents 2,271,623; 2,288,226; 2,334,864, and of the polyethylene glycol type of U.S. Patent 2,866,437.

The neutral-image-forming coupler composition that is incorporated in the silver halide emulsion of our equivalent-neutral-density-image-forming layer contains a coupler or mixture of couplers which, under conditions of normal color processing including bleaching treatment, produce a substantially equivalent-neutral-printing image comprising a dye (or a mixture of dyes) whose combined colors produce a substantially neutral image. Usually a mixture of two or three color-forming couplers is used to produce the neutral dye image. For example, a mixture of a red-dye-forming coupler and a cyan-dye-forming coupler; a mixture of a blue-dye-forming coupler and a yellow-dye-forming coupler; or a magenta-dye-forming coupler, a cyan-dye-forming coupler, and a yellow-dye-forming coupler, can be used to advantage. The appropriate proportions of the couplers used in such mixtures will depend upon the reactivities of particular couplers used, the particular developing agent used, the absorption characteristics of the dyes formed, etc., and can be determined readily by methods well known in the art.

The particular coupler or couplers used are not critical as long as an equivalent-neutral-printing image is formed under conditions of color processing, including a normal silver bleaching treatment. Any of the well known nondiffusing couplers are used to advantage. Typical couplers may be found, for example, in the following U.S. patents.

Cyan.—2,895,826, Salminen et al., July 21, 1959; 2,474,293, Weissberger et al., June 28, 1949; 2,908,573, Bush et al., October 13, 1959, phenols or naphthols.

Cyan: 2,423,730, Salminen et al., July 8, 1947, phenols.

Magenta: 2,600,788, Loria et al., June 17, 1952, 2,908,573, Bush et al. Oct. 13, 1959, 5-pyrazolones.

Yellow: 2,875,057, McCrossen et al., Feb. 24, 1959, 2,908,573, Bush et al., Oct. 13, 1959, open chain couplers.

Couplers producing red images

4 - [α-(2,4-di-t-amylphenoxy)butyramido]cyenoacetylbenzene.

4 - [γ-(3-pentadecylphenoxy)butyramido]cyanoacetylbenzene.

4-[γ-(3-pentadecyl-x-sulfophenoxy)butyramido]cyanoacetylbenzene

Similarly, other cyanoacetylbenzene couplers having appropriate ballasting group substituents are used to advantage as red-image-producing couplers in our neutral-die-forming coupler composition.

Couplers producing blue images

2 - [γ - (2,4-di-t-amylphenoxy)butyramido]-5-hexaneamidophenol.

2-benzamido-5-[γ-(2,4-di-t-amylphenoxy)butyramido]-phenol.

Similarly, other blue-dye-forming couplers described in Salminen and Barr U.S. Patent 2,772,162, issued Nov. 27, 1956, are used to advantage as blue-image-forming couplers in our neutral-dye-forming coupler composition.

Typical neutral-dye-forming coupler compositions that are used to advantage include the following mixtures:

4 - [α - (2,4-di-t-amylophenoxy)butyramido]cyanoacetylbenzene and 5-(p-amylphenoxybenzenesulfonamido)-1-naphthol;

4 - [γ-(3-pentadecylphenoxy)butyramido]cyanoacetylbenzene and 2-benzamido-4-chloro-5-methylphenol;

4 - [γ-(3-pentadecylphenoxy)butyramido]cyanoacetylbenzene and 5-(p-amylphenoxybenzenesulfonamido)-1-napthol;

2 - [γ - (2,4-di-t-amylphenoxy)butyramido]-5-hexaneamidophenol and α-(p-benzoylbenzoyl)acetanilide;

2 - [γ - (2,4-di-t-amylphenoxy)butyramido]-5-hexaneamidophenol and N-(4-benzoylacetamidobenzenesulfonyl)-N-benzylaniline;

2-benzamido-5-[γ-(2,4-di-t-amylphenoxy)butyramido]-phenol and α-(p-benzoylbenzoyl)acetanilide;

5-(p-amylphenoxybenzenesulfonamido)-1-naphthol, 1-phenyl-3-acetamido-5-pyrazolone and α-(p-benzoylbenzoyl)acetanilide;

2 - (4''-t-amyl-3'-phenoxybenzamido)3,5-dimethylphenol, 1 - (2',4',6'-tribromophenyl)-3-benzamido-5-pyrazolone and N,N'-di-(acetoacetamido)diphenyl;

2 - benzamido - 4-chloro-5-methylphenol, 1-phenyl-3-benzamido-5-pyrazolone and α-benzoyl-4-(N-benzyl-N-phenylsulfamyl)-acetanilide;

2-benzamido-6-chloro-5-methylphenol, 1-phenyl-3-acetamido-5-pyrazolone and α-(p-benzoylbenzoyl)acetanilide;

2 - (4''-t-amyl-3'-phenoxybenzamido)-2,5-dimethylphenol, 1-phenyl-3-acetamido-5-pyrazolone, and α-(p-benzoyl)acetanilide; etc.

The color-forming couplers can be incorporated in the neutral-image-forming layer by using coupler solvents and coupler-solvent dispersing techniques for incorporating couplers, such as described in U.S. Patents 2,322,027; 2,801,171; 2,949,360, etc. Among the useful high-boiling crystalloidal coupler solvents are (1) alkyl esters of

phthalic acid, e.g., methyl phthalate, dioctyl phthalate, etc.; (2) esters of phosphoric acid, e.g., tricresyl phosphate, etc.; (3) alkyl amides or acetanilides, e.g., N-butylacetanilide, etc. Low-boiling, water-insoluble solvents include esters, e.g., ethyl acetate, ethyl propionate, etc., alcohols, e.g., sec. butyl alcohol, halohydrocarbons e.g., carbon tetrachloride, etc. Watersoluble organic solvents used to advantage include compounds such as methyl isobutyl ketone, β-ethoxyethyl acetal, methyl Cellosolve acetate, acetonyl acetone, etc.

Our silver halide emulsions containing the neutral-dye-forming coupler composition are coated advantageously over the outer light-sensitive layer of the multicolor photographic element by any of the well-known coating methods. A protective gelatin overcoat may be applied.

Any of the multilayer, multicolor photographic element by any of the well-known coating methods. A protective gelatin overcoat may be applied.

Any of the multilayer, multicolor photographic silver halide elements that contain the incorporated color-forming couplers necessary for the color image formation are used to advantage according to our invention. The preferred elements have camera speed emulsions. Usually the multicolor element contains three silver halide emulsion layers containing different color-forming couplers and each layer being sensitive to light from a different third of the visible spectrum such that upon exposure to an original image and color development, each of the three layers produces a dye image having a color that is complementary to the color of light to which the said layer was sensitive. Ususally a blue-sensitive yellow-image-forming layer is outermost with a green-sensitive magenta-image-forming layer and a red-sensitive cyan-image-forming layer coating underneath in either order upon any suitable support, including cellulose acetate film, cellulose nitrate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials, as well as glass, paper, and others. Usually the element has a bleachable yellow (blue-light-absorbing) filter between the blue-sensitive layer and the light sensitive layers coated under it, as well as a bleachable antihalation layer. One or more of the color-image forming layers may be double coated or coated with a mixed emulsion, one emulsion being a highly sensitive component with a relatively coarse grain and the other, a less sensitive component with a relatively fine grain, such as one described in British Patent 923,045. The multicolor elements may have one image-forming layer that contains red-sensitive cyan image-forming packets, blue-sensitive yellow image-forming packets and green-sensitive magenta-image-forming packets, such as are described in Godowsky et al U.S. Patent 3,152,907.

Our silver halide emulsion layer with its neutral-dye-forming coupler composition cooperates with the multicolor element to produce the novel effects that make our photographic materials valuable. In the preferred forms, the said emulsion layer is sensitized to a different photographic speed than is the underlying color element.

In one preferred form, the overlying equivalent-neutral-image-forming layer is given a higher sensitivity to light (i.e., higher in speed) than the underlying layers with a contrast that is essentially the same so that the gradation of the neutral dye image ceases as the exposure becomes sufficient to expose the underlying color film. A variety of combinations of emulsion speed and coupler quantity may be used in our equivalent-neutral-image-forming layer depending upon the desired result. Our film can be processed advantageously in normal color negative processes to form an image entirely in the overlying layer for very low exposure levels, partly in the overlying layer and partly in the color layers for intermediate or wide range exposures, and entirely in the color layers for exposures of sufficient intensity. Our invention provides a valuable color film which will insure the user of a photograph even though there is insufficient light to obtain a photograph with color films previously available, and will produce high quality color photographs when there is sufficient light for color photography. This form of our invention provides a single film for use as a color negative or a black-and-white negative, depending upon the exposure, a film for night or other effect photography, a high speed negative with some discrimination, etc.

In another preferred form, our overlying equivalent-neutral-printing layer is made less sensitive to light (i.e., lower in speed) and more contrast than the underlying layers. Usually our overlying layer is sensitized so that it is slower than the color-image-forming layers by an amount that is approximately equal to the useful latitude of the color-forming layers. The range of latitude of the color negative element is from about 1.0 log E to about 2.5 log E, with the preferred range from about 1.4 log E to about 1.6 log E. Thus, in one of our preferred elements having a color negative latitude of about 1.5 log E, the neutral-dye-image-forming layer is advantageously about 1.25 log E slower than the color negative material. The contrast or gamma of our neutral-image-forming layer is higher than the contrast of the color negative material usually such that the overall combined gamma in the shoulder of the sensitometric curve is at least about 20% higher than the gamma of the color negative material alone.

The following examples will still further serve to illustrate our invention.

EXAMPLE 1

A multilayer color film was prepared as described in Example 16, part 1 of Carroll, Elins, Graham and Wilson U.S. Patent 2,944,900, issued July 12, 1960.

A silver bromoiodide gelatin emulsion having a higher contrast such that the combined contrast was approximately 50% higher than the contrast of the multilayer color film, and a threshold speed approximately 1.3 log E slower than that of the silver halide emulsions used in the multilayer color coatings was panchromatically sensitized with a thiocarbocyanine dye of the type described in Sprague U.S. Patent 2,503,776, issued Apr. 11, 1950. To this emulsion there were added 6 parts of a cyan coupler of the type described on page 1 of Salmanin and Weissberger U.S. Patent 2,423,730, 20 parts of a magenta coupler of the type described in Column 3 of Loria, Weissberger, and Vittum U.S. Patent 2,600,-788, and 14 parts of a yellow coupler of the type described in Column 5 of McCrossen, Vittum and Weissberger U.S. Patent 2,875,057. The concentration of each coupler was adjusted so that an equivalent neutral-printing dye image would be produced when the exposed emulsion was developed in a p-phenylenediamine type developer.

The multilayer color film described above was overcoated with the panchromatically sensitized silver bromoiodide gelatin emulsion containing the mixture of the three couplers.

A piece of the above described overcoated color negative was used to photograph a person and some printed material. The exposed film was processed through the following steps:

Solution		Time
(1)	Color developer ____ minutes__	12
(2)	Rinse ____ seconds__	10
(3)	Kodak F–5 fixing bath ____ minutes__	4
(4)	Wash ____ do____	4
(5)	Bleach (ferricyanide) ____ do____	8
(6)	Wash ____ do____	4
(7)	Kodak F–5 fixing bath ____ do____	4
(8)	Wash ____ do____	8

The various processing solutions had essentially the compositions set out below:

Color Developer:

Benzyl alcohol	ml	5.5
Sodium hexametaphosphate	g	2.5
Sodium sulfite desiccated	g	1.95
Sodium bromide	g	1.18
Sodium hydroxide	g	13.3
Borax	g	44.9
4-amino - N - ethyl-N-(β-methanesulfonamidoethyl) - m -toluidine sesquisulfate monohydrate	g	5.0

Water to make 1 liter.

Ferricyanide bleach:

Potassium ferricyanide	g	50.0
Sodium bromide	g	20.0
Borax	g	7.3
Boric acid	g	15.0

Water to make 1 liter.

The processed film had a good-quality negative color reproduction of the model as well as a good negative equivalent-neutral-printing reproduction of the printed material that had been photographed.

EXAMPLE 2

A multilayer, multicolor negative-type camera film similar to that used in Example 1 was overcoated with a panchromatically sensitized silver bromoiodide emulsion having the same contrast as that of the multilayer three-color emulsion and a threshold speed 1.3 log E faster than that of the multilayer three-color coating. The overcoat layer contained 150 mg./ft.^{2} of silver, 175 mg./ft.^{2} of gelatin, and a mixture of couplers was added to the coating melt as low ratio (1:½) coupler dispersions and coated at the following spread: 25 mg./ft.^{2} of the cyan-forming coupler of the type described on page 1 of U.S. Patent 2,423,730, to 12.5 mg./ft.^{2} of di-*n*-butylphthalate; 30 mg./ft.^{2} of the magenta-forming coupler of the type described in column 3 of U.S. Patent 2,600,788, to 15 mg./ft.^{2} of tricresyl phosphate; and 27 mg./ft.^{2} of the yellow-forming coupler of the type described by U.S. Patent 2,875,057, to 18.5 mg./ft.^{2} of di-n-butylphthalate.

The above described coating was then overcoated with a gelatin antiabrasion layer.

A sample of the above described overcoated color negative film was given a low level exposure to a light image and processed in accordance with the procedure given in Example 1 using the process solutions given in Example 1.

An equivalent-neutral-printing image was developed by processing the low-level exposed element.

A second sample of the element was given a high exposure (about 15 to 20 times that of the low level exposure) and processed as described to produce a conventional color image.

A third sample was given an intermediate level exposure. When processed as described, a combination of equivalent-neutral-printing and color image resulted having varying degrees of desaturation of the colors with effects resembling night photography.

Methods well known in the art are used to advantage to make positive prints of our negative reproductions.

Although the color developer solutions used in the above examples use 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate as the color developer, it is understood that any of the color developing agents used in color photography are used to advantage in the color development of our photographic material. These developing agents include N,N-dimethyl - p - phenylenediamine, N - carbamidomethyl-N - methyl - p - phenylenediamine, 3 - acetylamino - 4-aminodimethyl aniline, N - ethyl - N - (β - methylsulfonamidoethyl) - 4 - aminoaniline, N - ethyl - N - (β - methylsulfonamidoethyl) - 3 - methyl - 4 - amino aniline and salts of N - methyl-N-(β-sulfoethyl) - p - phenylenediamine, etc. Particularly useful color developing agents include 4 - amino - N - (β - sulfoethyl) - N - ethyl - 3-methyl - aniline, N,N - diethyl - p - phenylenediamine, 2 - amino - 5 - diethyl - aminotoluene, 4 - amino - N,N-diethyl - 3 - (β - methylsulfonamidoethyl) - aniline, 4-amino - N - (β - sulfoethyl) - N - ethyl - 3 - methoxy-aniline, 4 - amino - N - ethyl - N - lauryl - 3 - methyl-aniline, etc.

Our invention is still further illustrated by the accompanying drawing.

The drawing is a cross-sectional view of one of our photographic elements comprising support **11** coated with red-sensitive silver halide emulsion layer **12** containing a cyan-forming coupler, green-sensitive silver halide emulsion layer **13** containing a magenta-forming coupler, bleachable yellow colored filter layer **14**, blue-sensitive silver halide emulsion layer **15** containing a yellow-forming coupler and silver halide emulsion layer **16** containing a neutral-dye-forming coupler composition.

Our silver halide emulsion layers containing the neutral-dye-forming coupler composition are valuable for use as an overcoat over the outermost light-sensitive layer of a multilayer, multicolor photographic element containing incorporated couplers. The preferred elements contain a neutral-dye-image-forming layer having a speed that is different from the speed of the underlying multicolor element.

In one preferred form our neutral-dye-image-forming layer is faster than the underlying layers so that a black-and-white picture is formed upon development of the material when insufficient exposure is used to make a color picture, while a color picture is produced upon development of the normally exposed material and a combined black-and-while and color picture is developed from material exposed at intermediate levels.

In another form of our invention, the neutral-dye-image-forming layer is slower and more contrasty than the underlying layers. This material is valuable for use in applications when a highlight mask is required.

Although the invention has been described in considerable detail with reference to certain preferred forms thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A light-sensitive photographic element for color photography comprising a support coated with:

(1) a multicolor light-sensitive photographic unit containing silver halide emulsions with incorporated color-forming couplers, which upon exposure to an original image and color photographic processing, forms a negative color photographic reproduction of said original image, and

(2) a light-sensitive emulsion layer containing light-sensitive silver halide grains and an incorporated substantially neutral-density-forming coupler composition which upon exposure to an original image and color photographic processing forms a negative silver-bleach-resistant equivalent-neutral-printing image of said original image, said emulsion layer having a different photographic speed than the said multicolor unit, such that when the photographic speed of said emulsion layer is higher than the speed of the said multicolor unit, the contrast of the said emulsion layer and the contrast of the said multicolor unit are essentially the same, and such that when the photographic speed of the said emulsion layer is slower than the speed of the said multicolor unit, it is slower by an amount that is approximately equal to the useful exposure latitude of the said multicolor unit and the contrast of the said emulsion layer is higher than the contrast of the said multicolor unit.

2. A light-sensitive photographic element for color photography comprising a support coated with four light-sensitive silver halide emulsion layers, each of three of

said silver halide emulsion layers containing a different color-forming coupler and each of said three layers being sensitive to light from a different third of the visible region of the spectrum, such that upon exposure to an original image and color development, each of the three said layers produces a negative dye image having a color that is complementary to the color of the light to which the said layer was sensitive and the three dye images produced together form a negative color photographic reproduction of the original image, and the fourth of said silver halide emulsion layers containing a coupler composition such that upon exposure to an original image and color development, the fourth said layer produces a negative-silver-bleach - resistant equivalent - neutral - printing image reproduction of said original image to which it was exposed, the fourth said layer having a photographic speed that is different from the other three said layers such that when the photographic speed of the said fourth layer is higher than the speed of the other three of said layers, the contrast of the equivalent-neutral-printing image reproduction is essentially the same as the contrast of the negative color photographic reproduction in the other three of said layers so that the gradient of the said equivalent-neutral-printing image ceases as the exposure becomes sufficient to expose the other three of said layers, and such that when the photographic speed of the said fourth layer is slower than the photographic speed of the other three of said layers, it is slower by an amount that is approximately equal to the useful exposure latitude of the other three of said layers and the contrast of the image produced in the said fourth layer upon color development is higher than the contrast of the color image produced in the other three of said layers by color development.

3. A light-sensitive photographic element for color photography comprising a support coated with:

(1) a multilayer light-sensitive photographic unit containing silver halide emulsions with incorporated color-forming couplers, which upon exposure to an original image and color photographic processing forms a negative color reproduction of said original image, and

(2) a light-sensitive emulsion layer containing silver halide grains and incorporated color-forming couplers which upon exposure to an original image and color photographic processing form a negative-silver-bleach-resistant equivalent-neutral-printing image, said layer being coated over the outermost light-sensitive layer of the said multicolor element, said emulsion layer having a different photographic speed than the said multilayer unit, such that when the photographic speed of the said emulsion layer is higher than the speed of the said multilayer unit the contrast of the said emulsion layer and the contrast of the said multilayer unit are essentially the same so that the gradient of the said equivalent-neutral-printing image ceases as the exposure becomes sufficient to expose the said photographic unit, such that when the photographic speed of the said emulsion layer is slower than the photographic speed of the said photographic unit, it is slower by an amount that is approximately equal to the useful latitude of the said photographic unit and the contrast of the said equivalent-neutral-printing image is higher than the contrast of the said color reproduction.

4. A light-sensitive photographic element for color photography comprising a support coated with:

(1) a multicolor light-sensitive photographic unit containing incorporated color-forming couplers, which upon exposure to an original image and color photographic processing, forms a negative color photographic reproduction of said original image, and

(2) a panchromatically sensitive emulsion layer containing silver halide grains and an incorporated substantially neutral-density-forming coupler composition which upon exposure to an original image and color photographic processing forms a negative-silver-bleach-resistant equivalent-neutral-printing image of said original image, said emulsion layer having a different photographic speed than the said multicolor unit such that when the photographic speed of said emulsion layer is higher than the speed of the said multicolor unit the contrast of the equivalent-neutral-printing image and the contrast of the said color photographic reproduction are essentially the same and such that when the photographic speed of said emulsion layer is slower than the speed of the said multicolor unit, it is slower by an amount that is approximately equal to the useful latitude of the said multicolor unit and the contrast of the said equivalent-neutral-printing image is higher than the contrast of the said color photographic reproduction.

5. A light-sensitive photographic element for color photography comprising a support coated with:

(1) a multicolor light-sensitive photographic unit containing incorporated color-forming couplers, which upon exposure to an original image and color photographic processing, forms a negative color photographic reproduction of said original image, and

(2) a light-sensitive emulsion layer containing light-sensitive silver halide grains, an incorporated cyan-forming phenolic coupler, an incorporated magenta-forming 5-pyrazolone coupler and an open chain yellow-forming coupler such that upon exposure to an original image and color photographic processing, the said layer forms a negative-equivalent-neutral-printing image reproduction of the said original image, said emulsion layer having a different photographic speed than the said multicolor unit such that when the photographic speed of the said emulsion layer is higher than the speed of the said multicolor unit the contrast of the said equivalent-neutral-printing image and the contrast of the said color photographic reproduction are essentially the same, and such that when the photographic speed of the said emulsion layer is slower than the speed of said multicolor unit, it is slower by an amount that is approximately equal to the useful latitude of the said multicolor unit and the contrast of the said equivalent-neutral-printing image is higher than the contrast of the said color photographic reproduction.

6. In a multilayer multicolor photographic unit comprising color-image-forming silver halide emulsion layers containing color-forming couplers, the improvement comprising a light-sensitive photographic silver halide neutral-dye-image-forming layer containing at least one color-forming coupler coated over the outermost color-image-forming layer of the said multicolor photographic unit said neutral-dye-image-forming layer having a different photographic speed than the underlying color-image-forming layers such that when the photographic speed of the said neutral-dye-image-forming layer is higher than the speed of the said color-image-forming layers, the contrast of the said neutral-dye-image-forming layer and the contrast of the said color-image-forming layers are essentially the same, and such that when the photographic speed of the said neutral-dye-image-forming layer is slower than the speed of the said color-image-forming layers, it is slower by an amount that is approximately equal to the useful latitude of the said color-image-forming layers and the contrast of the said neutral-dye-image-forming layer is higher than the contrast of the said color-image-forming layers.

7. A process for producing a negative-color image and a negative-neutral-dye image in a light-sensitive photographic element for color photography comprising (1) a multilayer multicolor light-sensitive photographic unit containing incorporated color-forming couplers, which upon exposure and color photographic processing, form a color photograph, and (2) a light-sensitive layer containing at least one silver halide emulsion and an incorporated substantially neutral-density-forming coupler composi-

tion, said layer being coated over the outermost light-sensitive layer of the said multicolor unit, said light-sensitive layer (2) having a different photographic speed than the said multicolor unit (1) such that when the photographic speed of said light-sensitive layer (2) is higher than the speed of the said multicolor unit, the contrast of the said layer (2) and of the said unit (1) are essentially the same so that upon color processing the said neutral-dye-image produced in (2) has a gradient that ceases as the exposure becomes sufficient to expose the said multicolor unit, and such that when the photographic speed of the said layer is slower than the photographic speed of the said multicolor unit, it is slower by an amount that is approximately equal to the useful exposure latitude of the said multicolor unit and the contrast of the said emulsion layer is higher than the contrast of the said multicolor unit, said process comprising the steps of:

(A) exposing the said photographic element to a light image to produce latent images in the light-sensitive layers,

(B) contacting the said exposed photographic element with an aqueous alkaline color developer solution to produce a negative-color image and a negative-silver image in the said multicolor unit (1), and a negative-neutral-density image and a negative-silver image in the said layer (2) containing the said coupler composition, and subsequently

(C) removing the bleachable-silver images formed in step (B) and the residual silver halide in said element leaving the said negative-color-image and the said negative-neutral-density image in said element.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,497,350 Dated February 24, 1970

Inventor(s) Henry C. Yutzy and Daan M. Zwick

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 48, between "and-" and "ele-", delete "while" and substitute in its place --white--; line 53, between "and-" and "reproduction", delete "while" and substitute in its place --white--.

Column 3, line 45, between "auric" and "and", delete "trichloric" and substitute in its place --trichloride--; line 50, between "Patent" and ") or", delete "2,251,925" and substitute in its place --2,521,925--.

Column 5, delete superfluous lines 16 through 18.

Column 6, line 11, between "more" and "than", delete "contrast" and substitute in its place --contrasty--.

SIGNED AND
SEALED
OCT 8 - 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
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Commissioner of Patents