9	Ì	Europäisches Patentamt European Patent Office Office européen des brevets	Publication number: <b>0 A</b> 2	295 716 2
:	EUROPEAN PATENT APPLICATION			
<ul> <li>Application number: 88109778.6</li> <li>Int. Cl.<sup>4</sup> G03C 7/26 , G03C 1/84</li> <li>Date of filing: 20.06.88</li> </ul>				
43	<ul> <li>Priority: 18.06.87 JP 150320/87 06.08.87 JP 195222/87 21.08.87 JP 206589/87 11.05.87 JP 112608/88</li> <li>Date of publication of application: 21.12.88 Bulletin 88/51</li> <li>Designated Contracting States: DE FR GB NL</li> </ul>		<ul> <li>Applicant: FUJI PHOTO FILM CO., LTD. 210 Nakanuma Minami Ashigara-shi Kanagawa 250-01(JP)</li> <li>Inventor: Takahashi, Koji FUJI PHOTO FILM CO., LTD. No. 210 Nakanuma Minami-Ashigara-shi Kanagawa(JP) Inventor: Shiba, Keisuke FUJI PHOTO FILM CO., LTD. No. 210 Nakanuma Minami-Ashigara-shi Kanagawa(JP) Inventor: Muramatsu, Yukio FUJI PHOTO FILM CO., LTD. No. 210 Nakanuma Minami-Ashigara-shi Kanagawa(JP) Inventor: Taguchi, Seiichi FUJI PHOTO FILM CO., LTD. No. 210 Nakanuma Minami-Ashigara-shi Kanagawa(JP) Inventor: Taguchi, Seiichi FUJI PHOTO FILM CO., LTD. No. 210 Nakanuma Minami-Ashigara-shi Kanagawa(JP)</li> <li>Representative: Patentanwälte Grünecker, Kinkeldey, Stockmair &amp; Partner Maximilianstrasse 58 D-8000 München 22(DE)</li> </ul>	

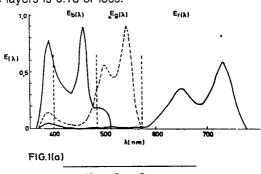
(54) Process for the formation of color image and band stop filter used therefor.

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A process for the formation of color images are disclosed wherein it comoprises printing on a color printing light-sensitive material comprising a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer provided on a support from a color print original in a subtractive exposure process, and then substantially subsequently color development, characterized in that the effective spectral sensitivity distribution of at least two light-sensitive layers in the light-sensitive layers of the color printing light-sensitive material are substantially independent from each other in a wavelength band of 400 to 750 nm and thereby the average color mixing degree in each said light-sensitive layers is 0.13 or less.



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#### EP 0 295 716 A2

#### PROCESS FOR THE FORMATION OF COLOR IMAGE AND BAND STOP FILTER USED THEREFOR

# FIELD OF THE INVENTION

<sup>5</sup> The present invention relates to a process for the formation of color images which comprises printing images on a color printing light-sensitive material from a color print original in a subtractive color exposure process, and then color-developing the color printing light-sensitive material. More particularly, the present invention relates to a process for the formation of color images which proves color reproducibility without deteriorating the conventional productivity, particularly without prolonged printing time.

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### BACKGROUND OF THE INVENTION

- In recent years, as multilayer color light-sensitive materials have been used for in color photograph, copying color originals, imaging or recording digital color data, etc., it has been desired to attain further excellent picture quality such as sharpness, graininess and color reproducibility, without deteriorating the productivity or rapidity in the process for the formation of images on silver halide color light-sensitive materials.
- In the system for the formation of positive-positive images by printing on a color reversal light-sensitive material or direct positive color light-sensitive material from color print originals such as transparent positive images obtained from photographing color reversal light-sensitive materials, color photographs obtained from instant photographic materials or color photographic papers, and color printed matters, color reproducibility faithful to color print originals has also been desired.
- In the system for the formation of so-called negative-positive images using photographing color lightsensitive materials and printing light-sensitive materials, many improvements to improve reproducibility of objects have been proposed applying advantageous conditions of color negative light-sensitive materials to photographing color light-sensitive materials. In particular, improvements have been made in three color dyes, blue-sensitive, green-sensitive and red-sensitive special sensitivity distributions, and color masking
- 30 process for correcting improper spectral absorption by three color dyes. Furthermore, attempts have been made to eliminate color mixture between emulsion layers having different color development to use DIR compounds to use a functional light-sensitive layer which has a different spectral sensitivity distribution of the light-sensitive layers from that of the above described light-sensitive layers in addition to the above described light-sensitive layers, etc. The details of such approaches are described in patents cited in
- Research Disclosure Nos. 17,643, and 18,717, U.S. Patent Nos. 2,407,210, 2,875,057, 3,265,506, 3,408,194, 3,447,928, 3,933,501, ,402,262, 4,401,752, 4,326,024, 4,310,619, 4,351,897, 3,061,432, 3,725,067, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 2,772,162, 3,758,308, 4,126,396, 4,334,011, 4,327,173, 3,446,622, 4,333,999, 4,451,559, 4,427,767, 4,163,670, 4,004,929, 4,138,258, 3,451,820, 4,080,211, 4,500,630, 4,540,654, and 4,367,282, Japanese Patent Publication Nos. 10,739/83, and
- 39,413/82, Japanese Patent Application (OPI) Nos. 43,659/85, and 34,541/86 (the term "OPI" as used herein means an "unexamined published application"), Research Disclosure Nos. 18,053, 24,220, and 24,230, British Patent Nos. 1,425,020, 1,146,368, and 2,102,173, West German Patent Application Nos. 2,219,917, 2,261,362, 2,329,587, 2,433,812, and 3,234,533, and European Patent Nos. 73,636, and 96,570.
- The spectral sensitivity distribution may be improved by the selection of a proper sensitizing dye or modification of crystal habit of particulate silver halide or process for the addition of particulate silver halide. However, such approaches are not necessarily enough.

The modification of spectral sensitivity distribution can be also accomplished by a use of a suitable photographic dye as described in Japanese Patent Publication No. 1,419/76, and West German Patent No. 1,015,683. However, such an approach is disadvantageous, because only the overlapped portion of spectral

sensitivity distribution of a specific layer and that of a layer other than the specific light-sensitive layer among a plurality of light-sensitive layers of a light-sensitive material is desensitized. Furthermore, such a photographic dye lowers sensitivity itself or has a desensitizing effect. Moreover, it is difficult for such a photo-graphic dye to be fixed on a predetermined layer. Such a photographic dye is also disadvantageous in that it tends to leave color after the formation of images. In particular, such a photographic dye often inhibit the spectral sensitization of silver halide emulsion brought by using a sensitizing dye. Improvements to fix tehse dyes in a predetermined layer also have been made. Such an approach are described in U.S. Patent Nos. 3,247,127, 2,390,707, 2,255,077, 2,493,747, 2,843,486, 4,420,555, 2,548,564, 2,484,430, 3,148,061, and 3,756,814, and British Patent Nos. 506,385, 584,609, 685,475, and 850,281.

Improvements for color printing light-sensitive materials have been made to obtain faithful color reproducibility as well as excellent sharpness and graininess of images using an excellent print original obtained from an excellent photographing color light-sensitive material. Besides the improvement in photographing color light-sensitive materials, improvements have been made in color couplers and their color dyes and spectral sensitivity distribution in blue-sensitive, green sensitive and red-sensitive layers. Furthermore, efforts have been made to inhibit color mixture between various layers.

Improvements in printing light-sensitive materials are described in Research Disclosure No. 18,716.
 Suitable silver halide emulsions which can be used improve in spectral sensitivity distribution are described in Japanese Patent Application (OPI) Nos. 5,423/73, 149,345/84, and 119,344/84, and U.S. Patent No. 3,655,394. Suitable sensitizing dyes for this purpose and process for the use of these sensitizing dyes are described in Japanese Patent Application (OPI) Nos. 114,418/74, 139,323/76, 26,589/80, 28,738/83, 5,238/84, 48,756/84, 133,540/84, 196,749/85, 210,345/86, and 205,929/86, and U.S. Patent No. 4,183,756. Examples of improvements in color couplers are described in Japanese Patent Application (OPI) No.

105,229/83.

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However, these approaches is still insufficient, because the objective data obtained on photographing color light-sensitive materials cannot be fully transferred to prints to deteriorate faithful color reproducibility of the objective image. Such a defect becomes remarkable as the properties of color couplers for use in color printing light-sensitive materials and color images produced therefrom are improved.

This is also the case where images on a color print original obtained from a photographing reversal color light-sensitive material or dupe light-sensitive material are printed on a direct color positive light-sensitive material or reversal color light-sensitive material. However, for direct color positive light-sensitive materials or reversal color printing light-sensitive materials, no process for decreasing the overlapping of spectral sensitivity distribution of a light-sensitive layer with that of other light-sensitive layers by using a suitable photographic dye has been suggested.

Japanese Patent Application (OPI) No. 113,627/76 discloses a process using a suitable light filter to cut a copying light in a wavelength band of 500 nm in which the blue sensitivity and the green sensitivity of a copying paper overlap each other, when an original is copied. The object of the process if to decrease copy trials to obtain color balance of copy previously or to adjust deviation in color balance which is caused on getting color balance. However, this approach effexcts on only copying conditions by cutting both blue and green light in a wavelength band in which the blue sensitivity and the green sensitivity of a copying paper overlapeach other. If a light filter having a wide absorption wavelength range is used, the blue sensitivity and green sensitivity of a copying paper are lowered. To compensate for this disadvantage, a stronger light for copy is required. This results in an increase in the remaining color mixture.

Japanese Patent Application (OPI) Nos. 64,037/78 and 113627/76 disclose a printer which is provided with filters such that the respective spectral sensitivities of a color paper are matched to that of blue light, green light and red light receivers in order to facilitate the adjustment of exposure time for the color paper when printing is made on a color paper from a negative film.

However, these approaches disclosed in Japanese Patent Application (OPI) Nos. 113,637/76 and 64,037/78 contemplate stabilization of copying or printing process. Accordingly, it cannot be said that these approaches can satisfactorily improve the quality of images.

Processes for printing on a color printing light-sensitive material from a color print original include additive process and subtractive process. In the light of productivity, subtractive exposure process, particularly using a white light source has been commonly put into practical use. In particular, this process provides a high processing capability per unit input, advantageous procedure for stabilization of photographic properties, efficient use of a light source, high quality level of color images on a print, etc. This process also enables a rapid or unmanned printing process.

The subtractive process such as white light subtractive process have been widely used in the form of an autoprinter because it can provide a high productivity and rapidity. However, such a process is disadvantageous to be improved in the finish quality and its stability. In order to eliminate these defects, many approaches have been suggested.

For example, U.S. Patent No. 2,997,389 suggests the use of a filter having a spectral absorption band in a yellow region and between 465 nm and 490 nm during the printing of a color transparent image on a color printing light-sensitive material in the subtractive exposure process. The above described U.S. Patent also suggests that a filter comprising a ZnS layer and an MgF<sub>2</sub> layer may be preferably used. U.S. Patent No. 4,050,807 suggests the combined use of a subtractive color filter and a filter adapted to remove

wavelengths in which spectral sensitivity curves of a copying photographic paper cross each other during enlarging and printing of photographic images or copy printing in the subtractive process. Japanese Patent Application (OPI) No. 64,03778 suggests that an autoprinter for printing on a color paper from a color negative film may be provided with a filter adapted to cut light in a wavelength band of 460 to 540 nm and

- 5 a filter adapted to cut light in a wavelength band of 570 to 640 nm to unite the spectral sensitivity of the receptor in the autoprinter with the spectral sensitivity distribution of the color paper increasing an accuracy of the exposure control in the autoprinter. However, the latter two patents have no description about the constituting elements of such suitable filters.
- For known filters, approaches have been heretofore suggested to modify the spectral sensitivity of the color light-sensitive material used to provide a light for print adapted for the spectral sensitivity of the color light-sensitive material or the spectral sensitivity distribution in the receptor in the color printer. However, in order to improve the color reproducibility, it is necessary to consider the spectral absorption characteristics of each original color images such as yellow image, magenta image, and cyan image, in a color negative film or color slide. In processes for the exposure of a color light-sensitive material comprising at least three
- 15 light-sensi-tive layers, subtractive exposure process is advantageous in that it can be easily effected with a high rapidity, providing a high productivity. However, the subtractive exposure process is also disadvanta-geous in that it is difficult to conform the spectral intensity distribution of the exposing light source to the spectral sensitivity distribution of three light-sensitive layers and to the spectral absorption characteristics of the corresponding color originals or materials to be copied. A filter having a spectral absorption in a
- wavelength band out of an absorption wavelength band of 465 to 490 nm as described in U.S. Patent No. 2,997,389 or a filter having a spectral absorption in a wavelength band out of the wavelength in which the spectral sensitivity curves of a copying photographic paper cross each other as described in U.S. Patent No. 4,050,807 is often useful. Accordingly, it has been desired to develop a filter having sharp spectral absorption characteristics excellent in transparency and a transmission wavelength band which is not limited to these wavelength bands but can be freely selected.

If such a filter is used interposed between the light source in a printer and a color light-sensitive material as described in U.S. Patent No. 2,997,389 and Japanese Patent Application (OPI) No. 64,037/78, the deterioration of the filter due to the high illumination and heat from the light source causes a problem. Such a filter as described in the above described two U.S. Patents cannot stand the prolonged use for more

30 than one month. The use of such a filter may cause a change in the finish quality of a print obtained from a color light-sensitive material. Such a filter is mechanically mounted on and removed from the printer very often and is susceptible to be scratched.

Processes for image exposure such as photographing objects to be copied and copying or printing from a color original include three processes. In the first process, the entire surface of a color light-sensitive material is imagewise exposed at the same time. This process requires lens and a shutter. An exposing machine to be used in this process may have a simple construction. In this process, the exposure can be effected only once or several times (sequential exposure process). This process can provide an excellent picture quality. Ordinary cameras and autoprinters employ this process. The second process is a slit exposure process. In this exposure process, a slit moves across the light axis between the object to be

- 40 copied or color original and the color light-sensitive material to effect image exposure. The third process is a synchronous slit exposure process. In this exposure process, the object to be copied or color original and the color light-sensitive material are synchronously moved during image exposure. The exposing machines according to these processes are relatively small but are susceptible to uneven scanning or image distortion due to unevenness in the speed of synchronous movement or insufficient accuracy of synchronous
- 45 movement. In the above described simultaneous exposure process, a wide radiation angle is obtained. However, the filter used in this process is included in an interference filter of the kind which varies in spectral absorption characteristics depending on the angle of incidence of the light, causing unevenness in the finish quality of color prints. Therefore, it has been desired to develop a band stop filter which is particularly improved so as to provide a less radiation angle dependency of spectral absorption.

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### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a color image formation process which enables an improvement in fidelity of color reproduction of images on a color printing light-sensitive material without prolonged printing time, i.e., without substantially deteriorating the sensitivity of the color printing light-sensitive material.

It is another object of the present invention to provide a color image formation process which can provide a color photograph having an unprecedentedly excellent color reproducibility from an original for color print such as color negative, color slide and dupe without deteriorating the productivity or rapidness in development.

It is a further object of the present invention to provide a color image formation process which can 5 provide a color photograph having an unprecedentedly excellent color reproducibility by a subtractive color exposure process.

It is further more object of the present invention to improve the quality level of color images, particularly the fidelity in color reproduction on a print and provide a process for the formation of color images which can eliminate the above described disadvantages by using a specified band stop filter or a band stop filter layer when printing from a color negative, positive photograph or color original in the conventional white light subtractive exposure process or additive exposure process.

These and other objects of the present invention will become more apparent from the following detailed description and examples.

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These objects of the present invention are accomplished by a process for the formation of color images which comprises printing on a color printing light-sensitive material comprising a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer provided on a support from a color print original in a subtractive exposure process, and then substantially subsequent color development, characterized in that the effective spectral light amount distribution of at least two light-sensitive layers in various light-sensitive

layers in the color printing light-sensitive material are substantially independent from each other in a 20 wavelength band of 400 to 750 nm and thereby an average color mixing degree in each color image forming layer of color print is 0.13 or less. The inventors have found that an unprecedentedly excellent color reproducibility can be attained by printing with a filter interposed between the printing light source and the color printing light-sensitive material such that the distribution of the product of the spectral sensitivity

distribution of the color printing light-sensitive material and the specteral transmittance distribution of the 25 three primary colors, i.e., yellow, magenta and cyan in the color print original corresponding to the spectral sensitiavity distribution of each light-sensitive layer, i.e, blue-sensitive layer, green-sensitive layer and redsensitive layer in the color printing light-sensitive material is independent while optimizing the spectral absorptivity of colored images obtained from main couplers for the formation of images, and the spectral absorptivity of colored images obtained from main couplers incorporated in a photographing color light-30

sensitive material as a color print original.

The inventors have worked out the concept of average color mixting degree as defined hereinafter and found that when the color mixturing degree is 0.13 or less, an unprecedentedly excellent color reproducibility can be attained in the transferred images from a color print original to a color printing light-sensitive material.

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### BRIEF DESCRIPTION OF THE DRAWINGS

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Figs. 1(a), 2(a), 3(a) and 4(a) show the effective spectral sensitive energy distribution (or effective spectral light amount distribution) E ( $\lambda$ ) in various light-sensitive layers in comparative examples or in the present invention;

Fig. 5(a) shows a representation of a color print obtained in the present invention in CIE(L\*a\*b) color specification system.

Fig. 1(b) is the spectral sensitivity curve (shown at GL) of a green-sensitive layer in a color printing light-sensitive material used in Example 3 of the present invention and the spectral energy distribution curve (shown at P) of a printer used in the same example;

Fig. 1(c) is the spectral sensitivity (relative) curve of a color printing light-sensitive material to be used in the present invention; 50

Fig. 2(c) is the effective spectral sensitive light amount distribution in a comparative color printing light-sensitive material in an image formation system;

Figs. 3(c), 4(c), 5(c) and 8(c) show the effective spectral sensitive light amount distribution in a color printing light-sensitive material of the present invention in an image formation system;

Fig. 6(c) shows a representation of the effect of the present invention in a CIE color specification 55 system; and

Fig. 7(c) shows the spectral transmittance curve of a band stop filter or sharp cut filter to be used in the present invention;

Figs. 1(d), 2(d) and 3(d) show the spectral transmittance curve of filter Samples 1, 2 and 3 used to be in the present invention, respectively.

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### DETAILED DESCRIPTION OF THE INVENTION

The color print original used in the present invention is a color light-sensitive material for use in photographing such as color negative light-sensitive material, color reversal light-sensitive material, and instant photographic light-sensitive material, negative film or transparent positive film obtained from dupe color light-sensitive material, or color photograph or printed matter comprising a transparent or reflective support. These light-sensitive materials normally have an image comprising at least three primaries, i.e., yellow coloring material (Y), magenta coloring material (M) and cyan coloring material (C) on a support.

Examples of a color printing light-sensitive material of the present invention include color photographic paper, direct positive color light-sensitive material, and reversal color light-sensitive material.

The present invention may be preferably applied to the subtractive exposure process, particularly color image formation process comprising a printing process by means of an automatic printer using a white light source.

In the color printing light-sensitive material, it is necessary to receive image data such as color hue and graduation, independently, which each has different spectral absorption characteristics due to yellow, magenta and cyan coloring materials in a color print original. In the present invention, to this end, it is most desirable to receive data only in the vicinity of the maximum sensitivity wavelength of the yellow, magenta and cyan coloring light-sensitive layers in a color printing light-sensitive material (λbs.max, λgs.max and λrs.max respectively).

In the color printing light-sensitive material, and blue sensitive layer may substantially have a spectral sensitivity in a wavelength band of 400 to 485 nm, the green-sensitive layer may substantially have a spectral sensitivity in a wavelength band of 485 to 570 nm, and the red-sensitive layer may substantially have a spectral sensitivity in a wavelength band of 570 to 750 nm. The blue-sensitive layer may have a maximum sensitivity wave-length (λs max) of 400 to 470 nm, the green-sensitive layer may have a maximum sensitivity wavelength of 520 to 570 nm, and the red-sensitive layer may have a maximum sensitivity wavelength of 520 to 570 nm, and the red-sensitive layer may have a maximum sensitivity wavelength of 520 to 570 nm, and the red-sensitive layer may have a maximum

sensitivity wavelength of 600 to 740 nm.

The effective spectral light amount distribution of the present color printing light-sensitive material will be explained hereinafter. Assuming that the spectral transmittance distribution of coloring materials in a color print original such as color negative film is T ( $\lambda$ ), the spectral sensitivity distribution of a light-sensitive

<sup>35</sup> layer such as green-sensitive layer in a color printing light-sensitive material is  $S(\lambda)$ , and the energy distribution of the printing light is  $P(\lambda)$ , the effective spectral sensitive energy distribution E ( $\lambda$ ) in the light-sensitive layer is given by the equation (1-1):

 $E(\lambda) = S(\lambda) \bullet T(\lambda) \bullet P(\lambda) \quad (1-1)$ 

Accordingly, the effective sensitive light amount of, for example, the green sensitive layer is given by the equation (1-2):

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 $Eg = \int Sg (\lambda) \cdot Tm (\lambda) \cdot P (\lambda) d\lambda \qquad (1-2)$ 485

The effective spectral sensitive energy distribution given by the equation (1-1) is called effective spectral light amount distribution.

The present invention features that at least two of the effective spectral light amount distribution of a blue-sensitive layer (BL), a green-sensitive layer (GL) and a red-sensitive layer (RL) in a printing light-sensitive material, i.e., Eb ( $\lambda$ ), Eg ( $\lambda$ ) and Er ( $\lambda$ ), respectively, are substantially independent each other. In the present invention, it is preferred that at least Eg ( $\lambda$ ) and Er ( $\lambda$ ) or Eg ( $\lambda$ ) and Eb ( $\lambda$ ), preferably Eb

 $_{55}$  ( $\lambda$ ), Eg ( $\lambda$ ) and Er ( $\lambda$ ) each is substantially independent each other. In particular, if within a range of 10% or less, preferably 7% or less of the effective spectral light amount (Eb, Eg or Er) of a light-sensitive layer obtained by printing grey images from a color negative film obtained by photographing a grey object, are contained or not contained, the effective spectral light amounts of the other light-sensitive layers, or if within a range of only about 15% or less or preferably about 7% or less of the maximum value of the effective spectral light amount distribution (Eb ( $\lambda$ ), Eg ( $\lambda$ ) or Er ( $\lambda$ )) of a light-sensitive layer, effective spectral light amount distributions of the other light-sensitive layers are contained, the color mixture is not substantially definitely observed, and this means that the effective spectral light amount distribution in these light-sensitive layers are substantially independent.

For example, for the green-sensitive layer (GL) in a color printing light-sensitive material, if in a wavelength band of 485 to 570 nm Er ( $\lambda$ ) and Ef ( $\lambda$ ) are limited within a range of Eg ( $\lambda$ ) x 0.15 or less or there are no Er ( $\lambda$ ) and Eb ( $\lambda$ ), or if in a wavelength band of 485 to 570 nm Er and Eb are limited within a range of Eg x 0.10 or less or there are no Er and Eb, it can be said that the effective spectral sensitive light amount distribution Eg ( $\lambda$ ) of the green-sensitive layer is substantially independent from that of the other

light-sensitive layers.

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In order to improve color reproducibility, it is necessary that the coloring material to be used in the color printing light-sensitive material be particularly improved and the color development doesn't cause mixture on color images due to residual color, stain, poor desilvering, etc. Preferably, it is necessary that

15 the spectral sensitivity of a photographing color light-sensitive material be predetermined as described in Japanese Patent Application (OPI) No. 89,850/88. More preferably, it is necessary that a coloring material comprising a yellow coupler or magenta coupler be improved so as to have a block type spectral transmittance.

The silver halide emulsion to be incorporated in the present color printing light-sensitive material, particularly in GL or RL preferably doesn't have an inherent sensitivity in the wavelength band for BL and a longer wavelength band.

The present color printing light-sensitive material is formed of such a silver halide emulsion and spectrally sensitized in such a manner that Eb ( $\lambda$ ), Eg ( $\lambda$ ) or Er ( $\lambda$ ) of each light-sensitive layer is independent.

The blue-sensitive layer (BL) is not always required to be spectally sensitized due to an inherent sensitivity of silver halide, but it may be preferably spectrally sensitized in such a manner that the maximum inherent sensitive wavelength thereof is set at 460 nm or less, preferably the wavelength band for BL or less, to provide a high rapidness in color development or inhibit mixture. Preferably, in order to provide a wavelength λ<sub>smax</sub> of the maximum S(λ) of BL given by a J-type spectral sensitization, any suitable sensitizing dye selected from those represented by the general formula (I) explained later may be used.

In order to evaluate the color reproducibility, a Macbeth chart comprising 18 chromatic colors and 6 achromatic colors may be commonly used. Examples of such a Macbeth chart are described in C.S.M. MaCamy, "J. Appl. Phot. Eng.", Vol. 2, pp. 95-99, 1976.

In the present invention, such a Macbeth chart is used to define the average color mixing degree in a color printing light-sensitive material as described hereinafter. By setting the average color mixing degree thus defined at 0.13 or less, an unprecedentedly excellent color reproduction on a color printing lightsensitive material from a color print original can be attained.

In the color printing light-sensitive material, the green-sensitive layer generally tends to deteriorate the color reproducibility among the three light-sensitive layers, i.e., blue-sensitive layer, green-sensitive layer and red-sensitive layer. Therefore, the green-sensitive layer in the color printing light-sensitive material will be further described hereinafter. Assuming that the spectral transmittance distribution of a color negative material obtained by photographing color chart i is  $Ti(\lambda)$ , the spectral sensitivity distribution of the green-sensitive layer in a color printing light-sensitive material is  $S(\lambda)$ , and the energy distribution of a printing light source is  $P(\lambda)$ , the exposure of the green-sensitive layer for color chart i is given by the equation (2-1).

$$Ei = \begin{cases} 570 \\ S(\lambda) \cdot Ti(\lambda) \cdot P(\lambda) \cdot d\lambda \\ 485 \\ i = 1 \text{ to } 24 \end{cases}$$

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In general, printing is made in such manner that achromatic image having a middle density are printed to get achromatic image having a predetermined density on a color printing light-sensitive material. Accordingly, if the exposure amount Ei of the color charts are determined based on the exposure amount

 $E_{22}$  of achromatic chart (i = 22 an optical density is amount about 0.7) Hi defined by the following equation (2-2) can represent whether the color exposure amount Ei of chart i is larger or smaller; comparing with a standard of achromatic image.

 $Hi = Ei/E_{22}$  (2-2)

A spectral sensitivity distribution in a delta function form having a 5 nm width in the center of the main maximum sensitive wavelength of the green-sensitive layer is the most preferable spectral sensitivity distribution, and Hi at the main maximum sensitive wavelength is defined as Hi<sup>°</sup>,  $\alpha_i$  defined on the equation (2-3) represents the magnitude of the deviation of the exposure amount of color chart i from the ideal exposure amount.

10  $\alpha_i = Hi/Hi^{\circ}$  (2-3)

Accordingly, the color mixing degree on an exposure for printing or at the printing (hereinafter refer to the color mixing degree)  $\beta_i$  of color chart i can be defined as shown by the equation (2-4).

 $\beta_i = \alpha_i - 1.0$  (2-4)

Therefore, an average color mixing degree on an exposure for printing (hereinafter refer to the average color mixing degree) r can be defined by averaging the color mixing degree  $\beta_i$  of color chart i over 18 Macbeth chromatic charts as shown in the equation (2-5).

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The average color mixing degree of the blue-sensitive layer and the red-sensitive layer can be similarly defined and easily determined with the effective wavelength band set at 390 to 485 nm and 570 to 740 nm, respectively.

 $\gamma = \frac{1}{18} \times \frac{\Sigma}{i=1} |\beta i|$ 

According to the Inventors' study, with respect to a color printing light-sensitive material, the color mixing degree of each chromatic chart has a close relationship with the average color mixing degree. In the present invention, the degree of color mixture can be represented by the color mixing degree or

(2-5)

- average color mixing degree on an exposure for printing (at the printing) in each of the light-sensitive layers. When the average color mixing degree is 0.13 or less, preferably 0.12 or less, particularly 0.10 or less in each of the light-sensitive layers, an excellent color reproducibility can be attained. Alternatively, when the color mixing degree of a Macbeth chart Y (i = 16) of at least one light-sensitive layer of the color printing light-sensitive material is 0.44 or less, preferably 0.42 or less, particularly 0.40 or less, an excellent
- reproducibility can be attained. When there is no color mixture, the color mixing degree is 0.0. However, if the average color mixing degree is 0.03 or less, it can be said that there is substantially no color mixing degree.

In the present invention, the blue-sensitive layer, the green-sensitive layer and the red-sensitive layer all have 0.13 or less of average color mixing degree thus defined above.

- The silver halide light-sensitive emulsion generally absorbs light to provide a latent image or becomes light-sensitive in a wavelength band of less than about 540 nm for a silver bromoiodide emulsion, less than about 500 nm for a silver bromide emulsion, or less than about 420 nm for a silver chloride emulsion as described in T. H. James, "The Theory of the Photographic Process", 4th Ed., 1977, pp. 39-44. Therefore, the halogen composition of particulate silver halide and the process for the formation of crystalline particulate silver halide are important in the present invention.
- In the case of the blue-sensitive layer, the silver halide light-sensitive emulsion may or may not be subjected to spectral sensitization to obtain a blue-sensitive layer. The inherent spectral sensitivity distribution of the silver halide is an important factor to improve the color mixing degree. The shorter the wavelength band of the inherent spectral sensitivity distribution is the more advantageous is the effect.
- In the case of the green-sensitive or red-sensitive layer, a silver halide light-sensitive emulsion which has been spectrally sensitized may or may not be provided with a dye-containing layer such as a filter layer which is adapted to cut light in a blue-sensitive wave-length band. Such a green-sensitive layer or redsensitive layer may be provided on a support. Therefore, it is important to decrease the color mixing degree, especially, between the blue-sensitive layer and the green-sensitive layer or between the bluesensitive layer and the red-sensitive layer is lowered.
- In the present invention, a silver halide emulsion having a low silver iodide content or average silver bromide content is preferably incorporated in the silver halide emulsion layer, particularly in the bluesensitive layer and/or green-sensitive layer. Particularly, a silver halide emulsion layer having 2 mol% or

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less of layer average silver iodide content, or being free of silver iodide is preferably used. Furthermore, a silver halide emulsion layer having an average silver bromide content of 80 mol% or less is preferably used. According to the present invention in which at least two or three of effective spectral light amount

distributions Eb ( $\lambda$ ), Eg ( $\lambda$ ) and Er ( $\lambda$ ) are made substantially independent from each other color reproducibility is remarkably improved when the distribution of proper spectral sensitivity of the photographing color light-sensitive material to the object of the photographing color light-sensitive material to the object is fully improved by a suitable method as described in Japanese Patent Application (OPI) Nos. 34,541 86, 201,245/86, 158,779/87 and 89850/88 or a coloring material to be used in the color printing lightsensitive material, especially coupler is fully improved.

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As a method to attain the objects of the present invention, a suitable filter or a filter layer can be used. A suitable filter or a filter lay can be used to restrict the main sensitive wavelength band of the bluesensitive layer, the green-sensitive lauyer and the red-sensitive layer in the present color printing lightsensitive material to, for example, 400 to 485 nm, 485 to 570 nm, and 570 to 750 nm, respectively. However, if the spectral absorption distribution of the filter is broad or is not predetermined in a proper wavelength band, it may deteriorate color balance or color reproduction.

In the present invention, the average color mixing degree as defined above can be adjusted to 0.13 or less by providing a filter or a filter layer substantially between the light source and the light-sensitive layer in the color printing light-sensitive material when images are printed on the color printing light-sensitive material in a subtractive exposure process. Alternatively, the average color mixing degree as defined above can be adjusted to 0.13 or less by providing in combination a color printing light-sensitive material

comprising a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer as described above and the filter or filter layer as described above.

The filter which can be used in the present invention may be interposed between the light source for use in the subtractive exposure process and the concerned light-sensitive layer in the printing light-sensitive material. Any optical filter otherwise prepared, filter layer incorporated in a color print original or filter layer provided on the light source side in the concerned light-sensitive layer in a color printing light-sensitive material may be preferably used so long as it gives 0.13 or less for the degree of color mixture in the color printing light-sensitive material.

In the present invention, a filter having a spectral absorption band which substantially exists in a wavelength band excluding the band of ±20 nm, preferably ±15 nm of the maximum effective spectral light amount  $\lambda E_{max}$  of each light-sensitive layer is preferably interposed between the light source and the color printing light-sensitive material during the printing process. The terminology "substantially exists" means half the width value or three-fourths the width value is used in the spectral transmittance curve.

A filter having an absorption band in a wavelength band, e.g., of less than 400 nm, 485 to 525 nm, or 570 to 630 nm may be preferably used.

Furthermore, a filter layer previously provided on a color negative film or a filter layer provided on the top layer of a light-sensitive layer in a color printing light-sensitive material may be preferably used in combination with such a filter. In addition, it is important that within a range of the main sensitivity zone of the concerned light sensitive layer, which lies in a range of  $\lambda_{smax}$  (the maximum sensitive wavelength) ±20

40 nm, preferably λ<sub>smax</sub> ±30 nm, more preferably λE<sub>max</sub> (the maximum effective spectral light amount) ±15 nm, most particularly λE<sub>max</sub> ±20 nm, the other layers substantially have no spectral sensitivity. For example, the green-sensitive layer is not sensitive to the light within a range of the wavelength λbsmax ±20 nm to which range the blue-sensitive layer is sensitive. To this end, the green-sensitive layer may be subjected to a spectral sensitization process which gives a sharp spectral sensitivity distribution. Secondly, the green-sensitive layer may comprise a silver halide emulsion having substantially.no or low sensitivity in the above described wavelength band. This can apply to other light-sensitive layers.

As a suitable filter there may be preferably used a band cut filter which comprises a multilayer dielectric-compound thin film as described hereinafter.

The band stop filter to be used in the present invention is a solid filter which has been prepared by repeatedly applying a silicon oxide layer and an aluminum oxide layer on a transparent substrate.

As a suitable substrate there may be used a substrate capable of withstanding a heat treatment such as hot coating. Examples of such a substrate include quartz, glass, ceramics, and plastic. Preferred among these materials are silicon oxide containing materials such as quartz and glass. The thickness of the substrate is preferably in the range of 0.2 to 2 mm. The silicon oxide or aluminum oxide layer has a thickness of 300 to 5,000 Å. The silicon oxide layer and the aluminum oxide layer are alternately provided on the substrate.

The present band stop filter having any spectral absorption characteristics in the visible band can be obtained by providing a multilayer structure of silicon oxide layer and aluminum oxide layer having different

optical thicknesses (refractive index and thickness). Such a multilayer structure can provide a stabilized finish quality excellent in fastness to light, heat and scratch.

The filter has preferably 7 or more, more preferably 21 to 101, particularly 47 or more layers. The more, particularly more than 20, the number of layers is, the higher is the maximum absorptivity of the band stop

5 filter, and the sharper is the spectral absorption characteristics obtained in the specified wave length band. Such a multilayer structure can provide a less change in the spectral absorption characteristics due to a deviation of the angle of incidence from the axial direction in the band stop filter.

In the present filter, a protective layer having a thickness preferably greater than that of the other layers is provided at its top layer. Such a protective layer can be provided by applying preferably a layer of silicon oxide or aluminum oxide, more preferably a layer of silicon oxide, to a thickness of 500 Å to 1 µm. Such a protective layer having a greater thickness than the other layers can further improve the scratch resistance and chemically protect the multilayer film, providing a band stop filter excellent in strage ability.

Therefore, a suitable filter according to the present invention is a band stop filter which has been prepared by applying 5 or more layers, preferably 21 to 101 layers, on a substrate and providing a protective layer having a greater thickness than the other layers thereon.

The present band stop filter can be obtained by alternately depositing silicon oxide and aluminum oxide on a substrate. The deposition of the material can be accomplished by any common method such as vacuum deposition, PVD (Physical Vapor Deposition) process such as ion plating process, or CFD (Chemical Vapor Deposition) process such as plasma deposition process. The degree of vacuum is preferably in the range of 10<sup>-11</sup> to 10<sup>-4</sup> torr, particularly 10<sup>-6</sup> to 10<sup>-4</sup> torr with nitrogen gas or an inert gas such as argon and helium, optionally mixed with oxygen gas.

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- The layer structure, thickness and constituting material of the present stop filter can be determined by observing the section of the filter under an electron microscope or by ESCA.
- The process for the formation of color images on a silver halide color light-sensitive material comprises photographing an object or image exposure such as copying or printing from a color original, and then color-developing the silver halide color light-sensitive material. Particularly, the image exposure can be effected by any suitable method selected from the three processes (collective simultaneous exposure process, slit exposure process, and simultaneous slit exposure process), additive exposure process, and subtractive exposure process. The band stop filter according to the present invention can be effectively used in all these exposure processes, particularly in the subtractive exposure process.
- As a suitable silver halide color light-sensitive material for the present invention there can be preferably used a negative/positive or positive/positive working process printing color light-sensitive material such as color photographic paper, color reversal photographic paper, color reversal film, silver die bleach process color photographic paper, direct positive type color photographic paper, diffusion transfer type color
- 35 photographic paper, heat-developable diffusion transfer type color photographic paper or film. These color light-sensitive materials can be used to directly photograph objects. Therefore, the present band stop filter can be used for an exposing machine, printer, mini-laboratory system printer and copying machine by which these color light-sensitive materials are processed. The present band stop filter can be preferably used in place of a band stop filter or band cut filter as described in Japanese Patent Application Nos.
- 229,856/87, 223,053/87, 239,032/87, and 260,357/87. The present band stop filter can also be used for an exposing machine or autoprinter for printing on an ordinary color photographic paper in the white light subtractive process as described in Japanese Patent Application Nos. 146,542/87, 200,508/87, 146,544/87, 191,187/87, and 255,048/87.

The present band stop filter preferably has a maximum absorption wavelength, preferably an absorption wavelength band, in a wavelength band outside the maximum wavelength ±15 nm, preferably the maximum wavelength ±20 nm, in the maximum sensitiave wavelength or the effective spectral light amount distribution of the blue-sensitive layer, green-sensitive layer or red-sensitive layer in such a light-sensitive layer.

The present band stop filter preferably has a sharp spectral absorption. In its spectral transmittance curve, the ratio of a width of 1.4 value of spectral transmittance ( $W_{1/4}$ ) to a width of 3/4 value of spectral transmittance ( $W_{3/4}$ ) is in the range of 0.50 or more, preferably 0.60 or more, more preferably 0.75 or more. As described above, such spectral characteristics can be attained by properly arranging layer thicknesses and a multilayer structure of repeating layers.

As such a substrate material there may be commonly used glass, silicon, sapphire, quartz, or surfacetreated plastic film or plate. As suitable dielectrics there may be used dielectrics as described in Japan

Society for the Promotion of Science's No. 131 Thin Film Committee, <u>Handbook of Thin Film</u>, Ohm-sha, 1983, Chapter 2.2 on page 817 and Table 2.6 on page 820. Examples of such dielectrics include inorganic compounds such as silicon dioxide, aluminum oxide, tin oxide, zirconium oxide, titanium, zinc sulfide, silicon, germanium, and tellurium, metal such as silver, aluminum, neodymium, titanium, and thallium, and

organic dielectrics, particularly high molecular dielectrics as described in Japan Society for the Promotion of Science's No. 131 Thin Film Committee, <u>Handbook of Thin Film</u> Ohm-sha, 1983, Chapter 2.2 on page 817, such as polystyrene, polypropylene, polyimide, FEP (Fluorinated Ethylene Propylene Resin) teflon, and poly  $\gamma$ -benzyl glutamate. These dielectrics may be used in combination.

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A multilayer comprising 5 to 50 layers, optionally more layers, can be provided by repeatedly coating at least two dielectrics having different refractive indexes to a predetermined thickness. The design of such a multilayer is described in Japan Society for the Promotion of Science's No. 131 Thin Film Committee, <u>Handbook of Thin Film</u>, Chapter 4 on page 823, and Shiro Fujiwara, <u>Optical Thin Film</u>, 2nd ed., 1986, Kyoritsu Shuppan Co., Ltd., Chapter 6. Such a multilayer thin film can be prepared by the sputtering process, CVD film-forming process or vacuum evaporation process.

A suitable band stop filter to be used in the present invention has a narrow absorption band having a half value width on the spectral transmittance curve ( $W_{1/2}$ ) of preferably less than 60 nm, more preferably 10 to 60 nm. Furthermore, the present band stop filter has a minimum transmittance of preferably 30% or less, more preferably 20% or less, particularly 10% or less.

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Furthermore, a band stop filter preferably having a spectral transmittance of 70% or more and a lowest transmittance in spectral absorption band of preferably 20% or less, more preferably 10% or less, may be preferably has a shape coefficient  $W_{1/4}/W_{3/4}$  ( $W_{1/4}$  represents 1/4 of spectral transmittance, and  $W_{3/4}$  represents 3.4 of spectral transmittance) of 0.5 or more. Furthermore, a band stop filter having a spectral absorption in a wavelength band of 430 nm or less, 490 to 530 nm, or 570 to 630 nm.

The average color mixing degree in the present invention can widely vary depending on the sensitizing dye used, halogen composition, etc. However, since the average color mixing degree in each element can be adjusted to 0.13 or less in accordance with the present invention by providing a filter having a necessary spectral transmittance (calculated from the average color mixing degree), such a multilayer dielectricdeposited thin film is advantageous in that it can easily attain the present average color mixing degree.

- Another example of a suitable layer is a filter layer to be incorporated in a color negative light-sensitive material. This process is intended to provide the light-sensitive layer side or back side in the color negative light-sensitive material with a spectral absorption by a masking colored coupler. For example, such a filter layer may be provided as a nondecolorizable dye-containing filter layer. This process may also be intended to correct undesired absorption by color dyes incorporated in the color negative light-sensitive material.
- Such a filter layer can be formed using, a colored coupler which has been prepared by optimizing the spectral absorptivity of a conventional colored coupler so as to give 0.13 or less for the color mixing degree in a color printing light-sensitive material. As such a filter layer there can be used a filter layer comprising a colored coupler as described in U.S. Patent Nos. 2,852,370, 2,860,975, 2,841,678, and 3,184,307, French Patent No. 73,826, West German Patent Application Disclosure No. 2,125,220, Japanese Patent Application 35 (OPI) Nos. 45,732/72, 123,341/75, and 130,024/79, Japanese Patent Publication Nos. 19,889/73, and

21,565/73, and British Patent No. 755,458. Particularly preferred are colored couplers as described in the patent application 129,143/87.

Such a filter layer may be provided by dyeing a hydrophilic light-sensitive layer (which may serve as an antihalation layer at the same time) disposed between a support and the nearest light-sensitive layer in a color negative light-sensitive material, dyeing the back layer of the support, or dyeing the support itself. Particularly preferred dyes which can be used in such a dyeing can be selected from the group consisting of nondecolorizable dyes having a sharp spectral absorption in a wavelength band between the maximum spectral sensitivity of BL and GL in the color negative light-sensitive material, e.g., 485 to 530 nm, such as dyes described as specific examples in Japanese Patent Application (OPI) No. 45.237/85 (pages. 6 to 11).

Alternatively, a nondecolorizable dye having a sharp spectral absorption in a wavelength band between the maximum spectral sensitivity of GL and RL in the color negative light-sensitive material, e.g., 570 to 630 nm may be preferably used. Such a nondecolorizable dye can be selected from the group consisting of anthraquinone dye, triphenylmethane dye, cyanine dye, melocyanine dye, pyrazolonexazole dye, azo dye, phthalocyanine dye, indoaniline dye, and indigo dye. If the above described two types of filter layers are provided in combination, the printing by the subtractive exposure process can be effected as easily as in

the conventional process. This process can improve the color mixing degree without deteriorating the color reproducibility, sensitivity and sharpness of the color negative light-sensitive material.

Further example of a suitable filter layer is a filter layer incorporated in the color printing light-sensitive material. Such a filter layer may be a filter layer capable of being decolored after development, provided on the light source side in a predetermined light-sensitive layer. Suitable dyes which can be incorporated in such a filter layer can be selected from the group consisting of dyes described in Japanese Patent Publication Nos. consisting of dyes described in Japanese Patent Publication Nos. 1,419/76, and 10,187/80, Japanese Patent Application (OPI) Nos. 154,439/84 and 64,346/85, French Patent Nos. 1,108,788, 2,182,329

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and 3,514,450, and West German Patent No. 2,429,228. These dyes and a suitable method as described in Japanese Patent Application (OPI) Nos. 65,230/75, 56,345/86, and 19,842/87 can be used to provide the desired filter layer. Particularly, functional dyes as described in Japanese Patent Application No. 106,892/87 to the present applicant may be preferably used in the present invention.

In the present printing light-sensitive material, it is preferred that a suitable filter layer is used while the spectral sensitivity distribution in the silver halide emulsion to be incorporated in the blue-sensitive layer and or green-sensitive layer is shifted to a shorter wavelength band by reducing the average silver iodide content and average silver bromide content and the mutual color separation in the spectral sensitivity distribution in the blue-sensitive layer, green-sensitive layer and red-sensitive layer is improved by properly selecting sensitizing dyes.

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Another method to obtain the objects of the present invention includes using a light-sensitive material comprising a blue-sensitive layer containing a yellow coupler, a green-sensitive layer containing a magenta coupler and a red-sensitive layer containing a cyan coupler provided on a support and satisfying the following conditions A), B) and C)

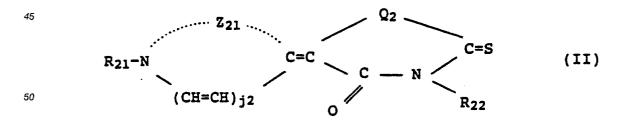
A) Silver halide emulsion used in the blue-sensitive layer and/or green-sensitive layer is an emulsion of silver chloride, silver bromide or silver chlorobromide containing 2 mol% or less (including 0%) of an average silver iodide content;

B) Silver halide emulsion used in the blue-sensitive layer is not spectrally sensitized or spectrally sensitized using at least one sensitizing dye selected from the group consisting of the compounds
 20 represented by the following formula (I) and (II).

C) Silver halide emulsion used in the green-sensitive layer is spectrally sensitized using at least one sensitizing dye selected from the group consisting of the compounds represented by the following formula (III).

25  $R_1 - N$  C = CH - C  $N - R_2$ (I) (CH = CH) j1
(CH = CH) k1 - (X\_1) n1
(X\_1) n1

<sup>35</sup> wherein Z<sub>1</sub> and Z<sub>2</sub> each represents a benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, benzooxazole nucleus, naphthoimidazole nucleus, benzooxazole nucleus, naphthoimidazole nucleus, indolenine nucleus, benzoindolenine nucleus, indole nucleus or guinoline nucleus which may be substituted; R<sub>1</sub> and R<sub>2</sub> each represents an alkyl group, alkenyl group, alkynyl group or aralkyl group; either or both of R<sub>1</sub> and R<sub>2</sub> each has at least one sulfonic acid group, carboxyl group or hydroxyl group; j<sub>1</sub> and k<sub>1</sub> each represents an integer of 0 or 1; n<sub>1</sub> represents an integer of 0 or 1; and X<sub>1</sub><sup>-</sup> represents an acid anion, with the proviso that when n<sub>1</sub> is 0, it indicates that an intramolecular salt is formed.



wherein Z<sub>21</sub> has the same meaning as Z<sub>1</sub> or represents a thiazole nucleus, selenazole nucleus, oxazole nucleus, imidazole nucleus, thiazolizine nucleus, thiazoline nucleus, benzothiazoline nucleus, naphthothiazoline nucleus, selenazolizine nucleus, selenazoline nucleus, benzoselenazoline nucleus, naphthoselenazoline nucleus, benzooxazoline nucleus, naphthooxazoline nucleus, benzimidazoline nucleus, naphothoimidazoline nucleus, pyrroline nucleus, pryridine nucleus, dihydroprydine nucleus, dihydroquinoline

nucleus, benzoimidazoline nucleus or naphthoimidazoline nucleus which may be substituted;  $Q_2$  represents a sulfur atom, oxygen atom, selenium atom or >N-R<sub>23</sub>; R<sub>21</sub>, R<sub>22</sub>, and R<sub>23</sub> each has the same meaning as R<sub>1</sub>; and j<sub>2</sub> has the same meaning as j<sub>1</sub>.

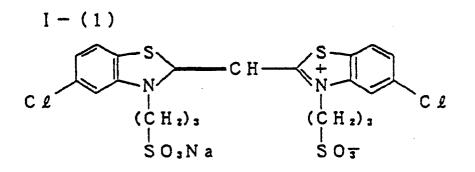
- In the general formulae (I) and (II), the heterocycle formed by Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>21</sub> may contain a substituent such as halogen atom, e.g., F. CI and Br, lower alkyl group, e.g., methyl group, ethyl group, trifluoromethyl group, benzyl group, phenethyl group, hydroxyl group, and alkoxy group, acetyl group e.g., phenyl group, chlorophenyl group, carboxyl group and estrified carboxyl group, carbamoyl group, and sulfamoyl group. Particularlly, a group which particularly forms a J-band, halogen atom, trifluoromethyl group, aryl group, and estrified carboxyl group may be preferably used.
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- As  $R_1$ ,  $R_2$ ,  $R_{21}$ ,  $R_{22}$  or  $R_{23}$  there can be used a group commonly used for cyanine dye, such as  $C_{1-6}$  lower alkyl group, alkoxyalkyl group, acetoxyalkyl group, alkylureidoalkyl group, hydroxyalkyl group, chloroalkyl group, sulfoalkyl group, carboxyalkyl group, allyl group, benzyl group, and phenethyl group. A combination of a compound represented by the general formula (I) and a compound represented by the general formula (II) may be used.
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Specified examples of compounds represented by the general formulae (I) and (II) will be shown hereinafter. However, the present invention should not be construed as being limited to these examples.

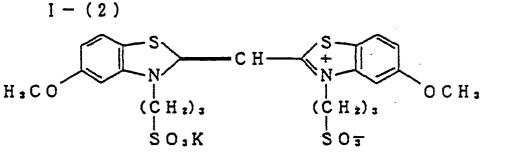




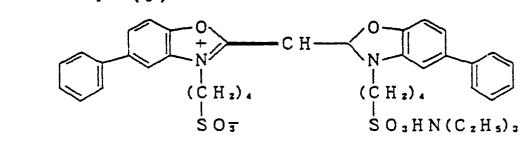
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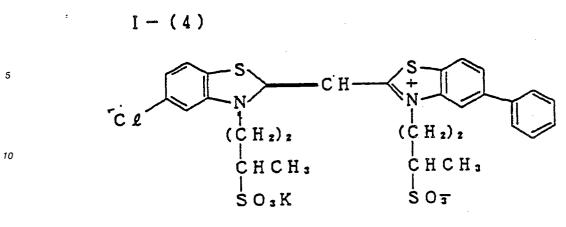
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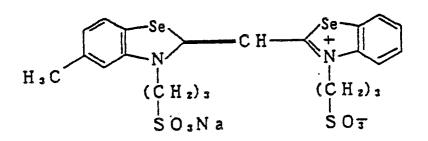
I - (3)



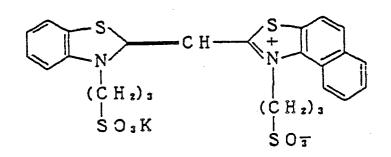
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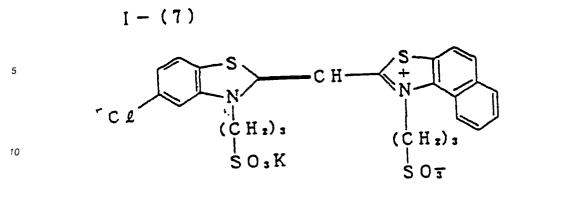


1-(5)

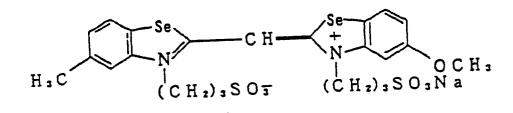


I - (6)

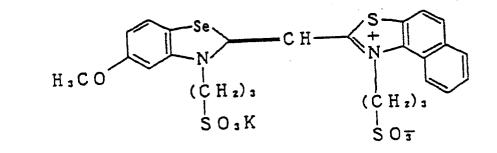




<sup>15</sup> I - (8)

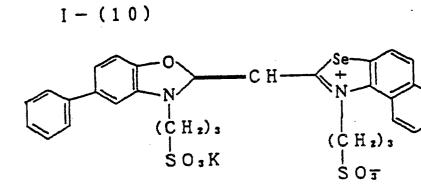


I - (9)

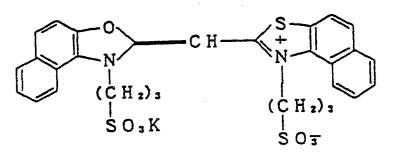




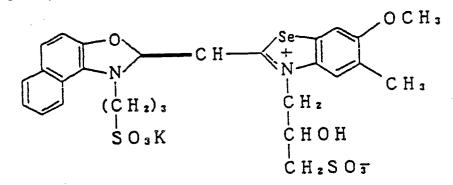


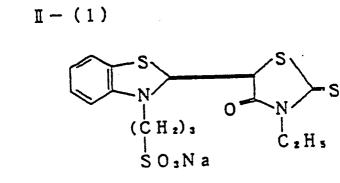


I - (11)

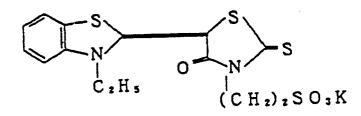


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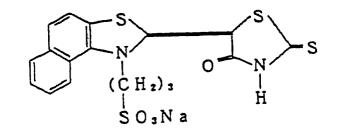




II- (2)



I- (3)



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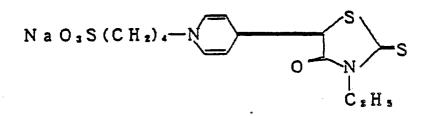


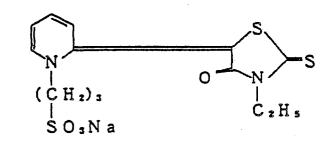
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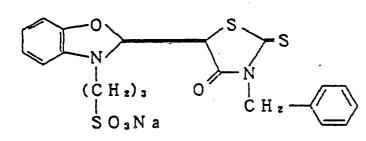




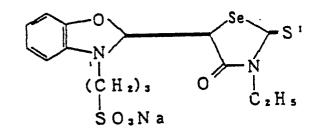




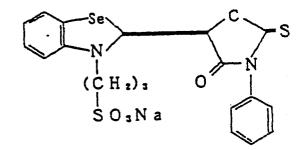
- (6)



I - (7)



I - (8)



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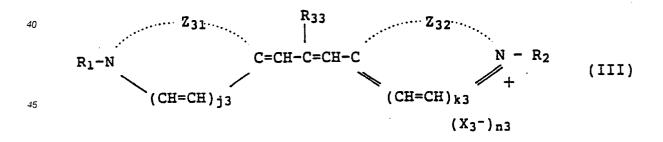
The amount of the compound of the general formula (I) and/or (II) to be incorporated in the bluesensitive layer is not specifically limited but is normally in the range of  $10^{-6}$  to  $1 \times 10^{-2}$  mol, preferably 5 x  $10^{-5}$  to  $2 \times 10^{-3}$  mol per 1 mol of silver halide.

Furthermore, a sensitizing dye which is strongly spectrally sensitized in a wavelength band of 485 to

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570 nm, preferably about 520 nm, to 570 nm, particularly 530 nm to 570 nm may be preferably incorporated in the green-sensitive layer. A silver halide emulsion wherein inherent sensitivity of silver halide has been shifted to a short wavelength band shorter than 420 nm by using low silver iodide and silver bromide content silver halide particles may be preferably incorporated in the green-sensitive layer. In particular, a silver halide emulsion which is sensitized in a J-band may be preferably incorporated in the green-sensitive layer. Preferred examples of such a compound include those represented by the general formula (III):

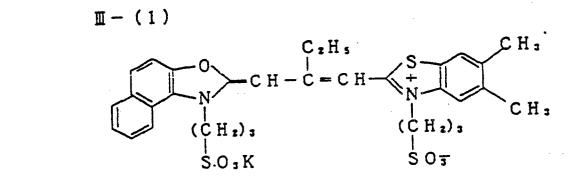


wherein Z<sub>31</sub> has represents benzimidazole nucleus, benzooxazole nucleus, naphthoimidazole nucleus or naphthooxazole nucleus; Z<sub>32</sub> represents benzimidazole nucleus, naphthoimidazole nucleus benzooxazole nucleus, naphthooxazole nucleus, benzothiazole nucleus or benzoselenazole nucleus which may be substituted; R<sub>31</sub> and R<sub>32</sub> each has the same meaning as R<sub>1</sub> and R<sub>2</sub> in the general formula (I); R<sub>33</sub> represents a hydrogen atom, lower alkyl group or aralkyl group; j<sub>3</sub> and k<sub>3</sub> have the same meaning as j<sub>1</sub> in the general formula (I); n<sub>3</sub> has the same meaning as n<sub>1</sub> in the general fromula (I); and X<sub>3</sub><sup>-</sup> represents an acid anion.

Examples of suitable substituents which can be contained in the heterocycle formed by  $Z_{31}$  and  $Z_{32}$  in the general formula (III) include those described a suitable substituents for heterocycle formed by  $Z_1$ ,  $Z_2$  and  $Z_{21}$  with reference to the general formulae (I) and (II).

Specific examples of the compound represented by the general formula (II) will be shown hereinafter,

but the present invention should not be construed as being limited thereto.



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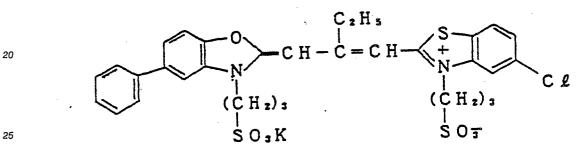
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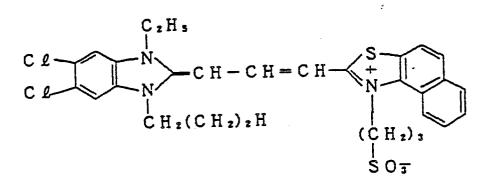
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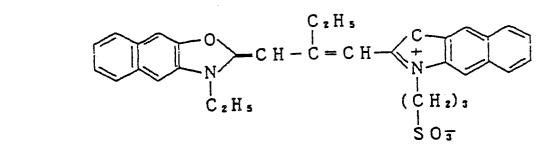
Ⅲ-(2)

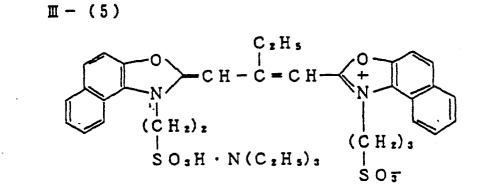


Ⅲ— (3)

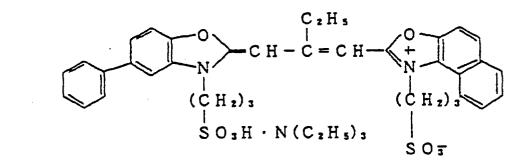
Ⅲ-(4)



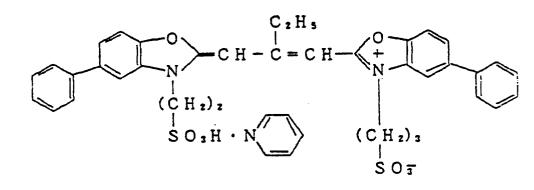






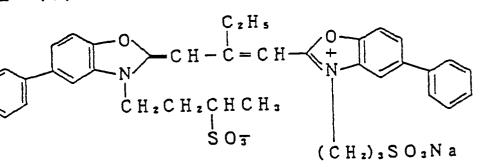


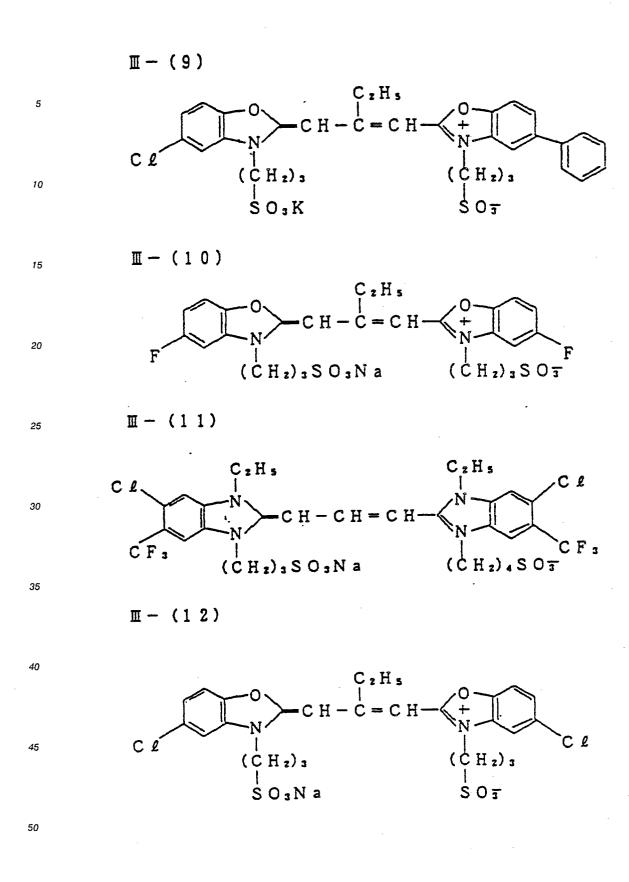
Ⅲ- (7)



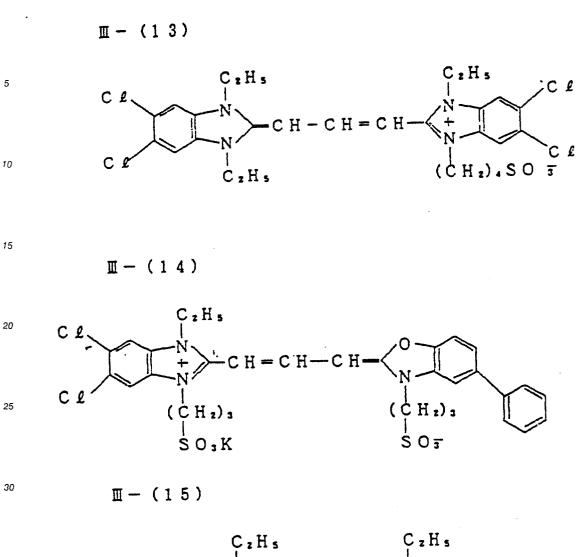
Ⅲ— (8)

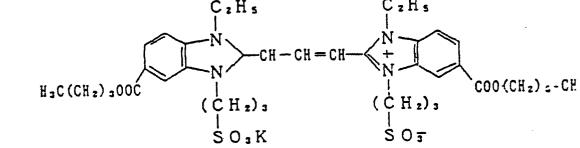






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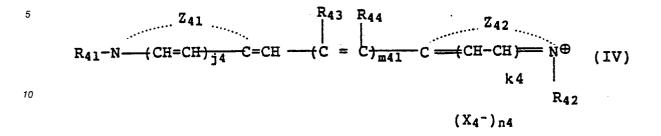
The amount of the compound of the general formula (III) to be incorporated in the green-sensitive layer is not specifically limited but is normally in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-2}$  mol, preferably  $5 \times 10^{-5}$  to  $2 \times 10^{-3}$  mol per 1 mol of silver halide. Two or more sensitizing dyes of the general formula (III) may be incorporated in combination in the green-sensitive layer.

As described above, a silver halide emulsion having a low silver iodide content or low silver a bromide content may be advantageously incorporated in the green-sensitive layer to inhibit color mixture with the blue-sensitive layer.

The red-sensitive layer is spectrally sensitized with a sensitizing dye which gives a strong spectral sensitization in a wavelength band where the spectral absorption by a magenta dye is not observed, e.g., wavelength band of longer than 600 nm, preferably 630 nm, depending on the spectral absorption by a cyan dye in the color negative original. A silver halide emulsion as described above may be preferably incorporated in the red-sensitive layer to inhibit overlapping with the blue-sensitive layer.

Spectral sensitization preferably carried out so that an average color mixing degree with blue sensitive layer and a color mixing degree with green sensitive layer is each less than 0.13.

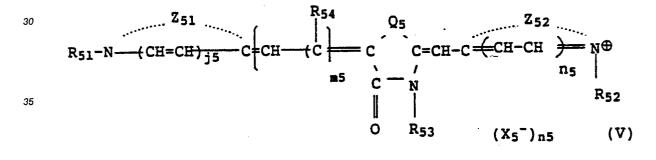
The red-sensitive layer to be used in the present invention may be preferably spectrally sensitized with a sensitizing dye represented by the general formula (IV), (V), or (VI).



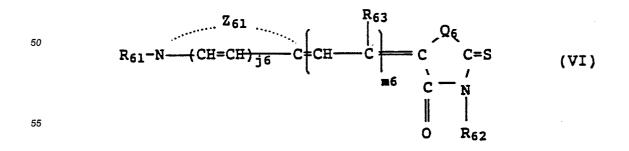
<sup>15</sup> wherein Z<sub>41</sub> and Z<sub>42</sub> each represents a 5- or 6-membered heterocyclic nucleus such as thiazole nucleus, <sup>15</sup> benzothiazole nucleus, naphthothiazole nucleus, selenazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, oxazole nucleus, benzooxazole nucleus, naphthooxazole nucleus, imidazole nucleus, benzimidazole nucleus, naphthoimidazole nucleus, 4-quinoline nucleus, pyrroline nucleus, pyridine nucleus, tetrazole nucleus, indolenine nucleus, benzindolenine nucleus, indole nucleus, tetrazole nucleus, benzotel-

razole nucleus, and naphthotelrazole nucleus; R<sub>41</sub> and R<sub>42</sub> each represents an alkyl group which may be substituted by a substituent such as halogen atom, cyano group, alkoxy group, substituted or unsubstituted amino group, carboxylic acid group, sulfononic acid group, and hydroxy group; alkenyl group; alkynyl group or aralkyl group; m<sub>41</sub> represents an integer of 1 to 3; j<sub>4</sub> and k<sub>4</sub> each represents an integer of 0 to 1; X<sub>4</sub> represents an acid ion; and n<sub>4</sub> represents an integer of 0 or 1, with the proviso that when m<sub>41</sub> is 1, R<sub>43</sub> represents a hydrogen atom, lower alkyl group, aralkyl group or aryl group and R<sub>44</sub> represents a hydrogen atom, lower alkyl group or aralkyl group or aralkyl group or aralkyl group, and R<sub>43</sub> may be connected to other R<sub>43</sub>'s to form a hydrocarbon ring or a

heterocyclic ring.



wherein Z<sub>51</sub> and Z<sub>52</sub> each has the same meaning as Z<sub>41</sub> or Z<sub>42</sub>; R<sub>51</sub> and Z<sub>52</sub> each has the same meaning as R41 or R<sub>42</sub>: R<sub>53</sub> represents an alkyl group, alkenyl group, alkynyl group or aryl group such as substituted or unsubstituted phenyl group; m<sub>5</sub> represents an integer of 0, 1 or 2; R<sub>54</sub> represents a hydrogen atom, lower alkyl group or aryl; Q<sub>5</sub> represents a sulfur atom, oxygen atom, selenium atom or >N-R<sub>55</sub> in which R<sub>55</sub> has the same meaning as R<sub>53</sub>; J<sub>5</sub>, R<sub>51</sub>, X<sub>5</sub><sup>Θ</sup> and n<sub>5</sub> have the same meaning as J<sub>4</sub>, K<sub>4</sub>, X<sub>4</sub><sup>Θ</sup> and n<sub>4</sub>, respectively, with the proviso that when m<sub>5</sub> represents 2, R<sub>54</sub> may be connceted to other R<sub>54</sub>'s to form a hydrocarbon ring or a heterocyclic ring which is preferably a 5- or 6-membered ring.



wherein Z<sub>61</sub> represents an atomic garoup required to form a heterocyclic ring (e.g. those as described with

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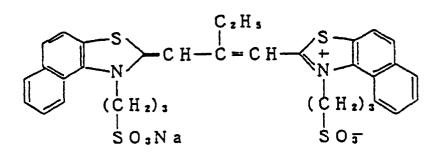
reference to  $Z_{41}$  and  $Z_{42}$ , such as thiazolidine, thiazoline, benzothiazoline, naphthothiazoline, selenazolidine, selenazoline, benzoselenazoline, naphthoselenazoline, benzosazoline, naphthooxazoline, dihydropyridine, dihydroquinoline, benzimidazoline, and haphthoimidazoline);  $Q_5$  has the same meansing as  $Q_5$ ;  $R_{61}$  has the same meaning as  $R_{51}$  or  $R_{52}$ ,  $R_{62}$  has the same meaning as  $R_{53}$ ;  $m_6$  has the same meaning as  $m_5$ ;  $R_{63}$  has the same meaning as  $R_{54}$ ; and  $j_6$  has the same meaning as  $j_5$ , with the proviso that when  $m_6$  is 2 or 3;  $R_{63}$  may be connected to other  $R_{63}$ 's to form a hydrocarbon or heterocyclic ring.

Specific examples of suitable sensitizing dyes which can be used in the present invention will be shown hereinafter.

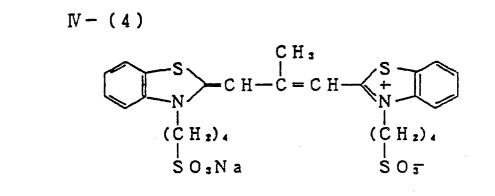
$$C \ell$$

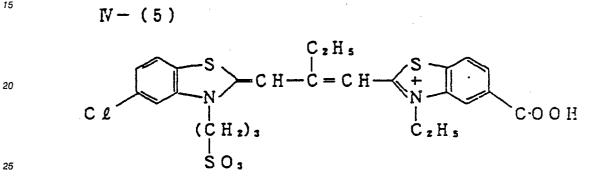
N - (1)

N - (2)

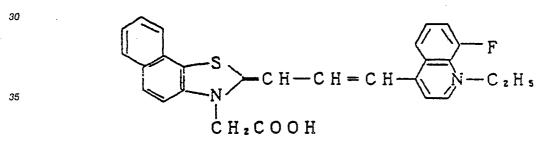


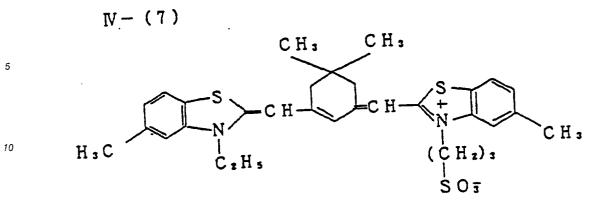
<sup>35</sup> N- (3)



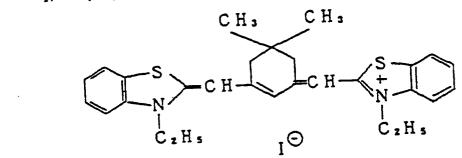


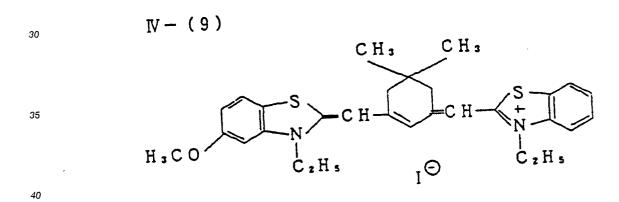
N-(6)

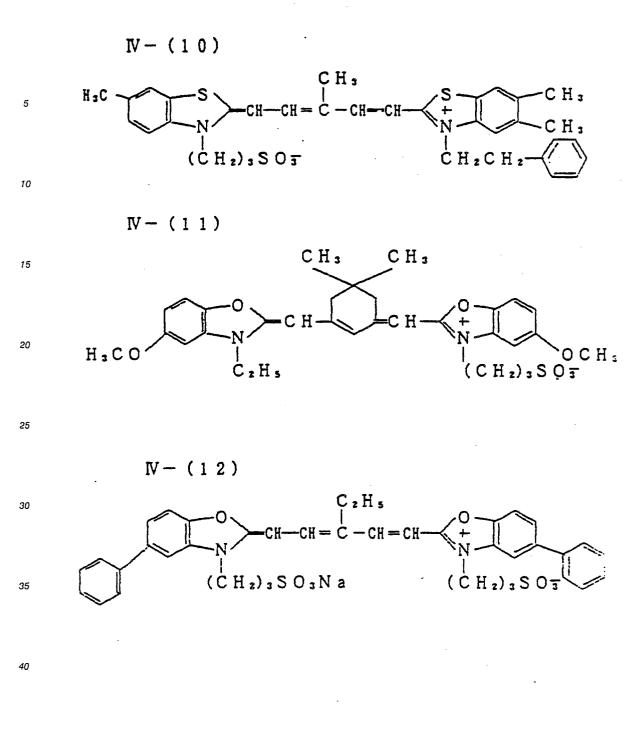


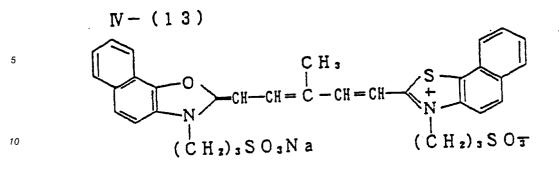


IV- (8)

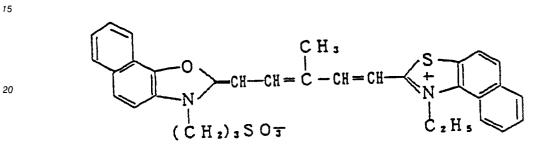




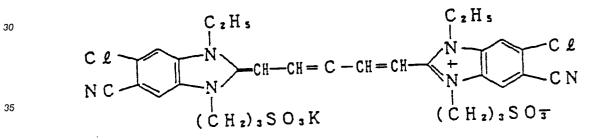


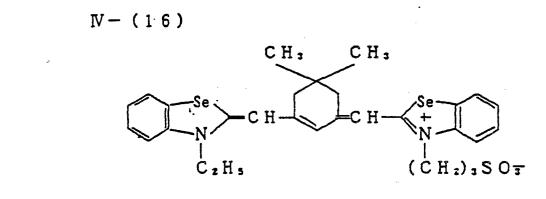


W - (1 4)



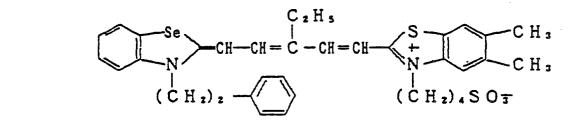
N - (15)



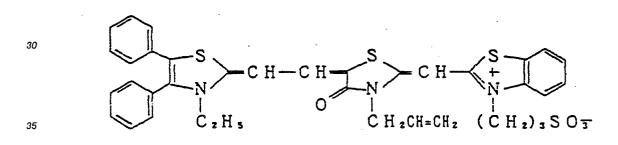


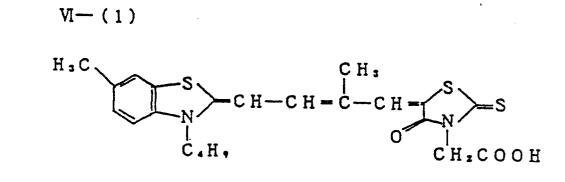
N - (17)



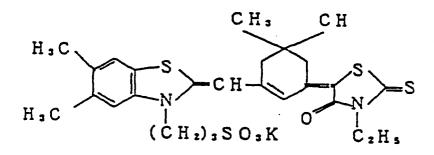


· V-(1)





VI - (2)



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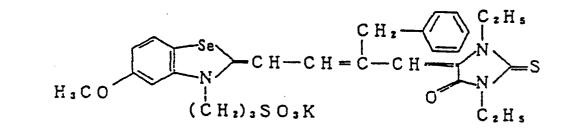
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VI- (3)



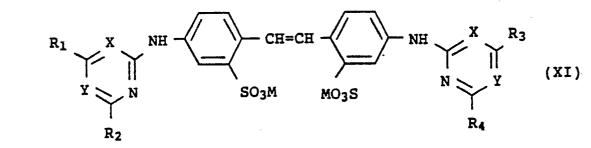
The sensitizing dyes of the present invention represented by the general formulae (IV), (V) and (VI) mkay be used in an amount of 1 x 10<sup>-6</sup> to 5 x 10<sup>-6</sup> to 1 x 10<sup>-3</sup> mol per 1 mol of silver halide, singly or in 40 combination with other susper sensitizers.

In the present invention, the spectral transmittance distribution  $Ti(\lambda)$  of a dye image obtained by the coupling reaction of a yellow, magenta or cyan coupler in a photographic color light-sensitaive material with a color developing agent affects the color mixing degree  $\beta$  or the layer average color mixing degree r as shown in Equation (2-1) or (2-5). a couler which provides an excellent color separation between dye images, particularly yellow and magenta may be preferably used.

These objects of the present invention may be accomplished by adjusting an average color mixing degree of color forming layer of a color printing light-sensitive material to be 0.13 or less by a process for the formation of color images which comprises printing on a color printing light-sensitive material from a color print original in a substactive exposure process, and subsequently color-developing said color pinting 50 light-sensitive material, characterized in that said color printing light-sensitive material comprises at least one blue-sensitive layer, at least one green-sensitive layer and at least one red-sensitive layer provided on a support, said green-sensitive layer has an effective spectral sensitive light amount distribution which is substantially formed by a J-type sepctral sensitization, said red-sensitive layer has an effective spectral sensitive light amount distribution which is substnatially formed by an M-type or J-type spectral sensitization, the effective spectral sensitive light amount distribution of said green-sensitive layer and said redsensitive layer, and/or the effective spectral sensitive light amount distribution of said green-sensitive layer and said blue-sensitive layer are substantially independent, and thereby the average color mixing degree on

an exposure for printing (at the printing) in each of said ligh-sensitive layers is 0.13 or less, and the color development process of said color printing light-sensitive material satisfies the following condition (A) and/or condition (B):

(A) at least one of color development, blix, and rinse and/or stabilization is carried out in the presence of at least one compound represented by the general formula (XI):



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wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each represents hydroxy group, halogen atom, heterocyclic amino group, heterocyclic thio group, alkoxy group, amino group, alkylamino group, aryloxy group or arylamino group; X and Y each represents = N- or = CH-; and M represents a monovalent cation, with the proviso that X and Y don't represent = CH- at the same time;

(B) the pH value of the bleaching or blix solution is in the range of 3.5 to 6.0 and the replenishing amount of the rinsing solution and/or stabilizing solution is 3 to 50 times the amount of said solution carried over from the pre-bath.

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Unlike the blue-sensitive layer and the green-sensitive layer, the red-sensitive layer (RL) can be more easily provided depending on  $T_{(\lambda)}$  of the coloring material in the color print original on a wavelength band longer than the wavelength band for the green-sensitive layer. Therefore, in order to make  $E_{r(\lambda)}$  independent from the other effective spectral sensitive energy distributions, any suitable sensitizing dye selected from those represented by the general formulas (IV), (V) and (VI) may be used to provide a maximum  $S_{(\lambda)}$  given by a J-type or M-type spectral sensitization. Sensitizing dyes represented by the general formulas (IV) may be used to give a J-type spectral sensitivity. Sensitizing dyes represented by the general formulas (V) and

(VI) may be used to give an M-type spectral sensitivity.

The spectral sensitization in the present color printing light-sensitive material essentially features a Jtype spectral sensitization or M-type spectral sensitization.

In the present invention, the effective spectral sensitive light volume distribution in the green-sensitive layer ( $E_{g(\lambda)}$ ) is given substantially by a J-type spectral sensitization, and the effective spectral sensitive distribution in the red-sensitive layer ( $E_{r(\lambda)}$ ) is given substantially by an M-type spectral sensitization or J-type spectral sensitization.

A J-type spectral sensitization is a sensitization by spectral absorption obtained by adsorption by J aggregates on a silver halide adsorbing substrate of a sensitizing dye. An M-type spectral sensitization is a sensitization by spectral absorption obtained by molecular adsorption by a sensitizing dye. Examples of these types of spectral sensitizations are described in T. H. James, "The Theory of the Photographic Process", 4th ed., 1977, pp. 218-222.

For examplke, if  $E_g(\lambda)$  is attributed to a J-type spectral sensitization, it means that  $E_g(\lambda)$  doesn't exhibit the maximum value of  $E_g(\lambda)$  corresponding to an M-type spectral esnsitization. If  $E_g(\lambda)$  is substantially attributed to a J-type spectral sensitization, it means that in the wavelength band for the green-sensitive layer the maximum value of  $E_g(\lambda)$  corresponding to an M-type spectral sensitization does not exhibit a value over the value of about one-second, preferably one-third the maximum value of  $E_g(\lambda)$  corresponding to a Jtype spectral esnsitization.

- <sup>50</sup> In accordance with the relationship between the effective spectral sensitive light volume distribution  $E_{(\lambda)}$  and the spectral sensitivity distribution  $S_{(\lambda)}$  in a color printing light-sensitive material determined by the equation (14), when  $S_{(\lambda)}$  is attributed to a J-type spectral sensitization,  $E_{(\lambda)}$  corresponding to the wavelength is normally attributed to a J-type spectral sensitization. Those skilled in the art can determine whether  $E_{(\lambda)}$ is attributed to a J-type spectral sensitization or M-type spectral sensitization from the structure of a sensitization dye used, the spectral absorption characteristics of the solution of the sensitizing dye, and the spectral absorption characteristics of the sensitizing dye adsorbed by silver halide. In general, the
- compound represented by the general formula (XI) has a strong effect of supersensitization for the M-type spectral sensitization of the present invention and thus tends to convert an H-type or J-type adsorption into an M-type adsorption. Those skilled in the art can understand if a spectral sensitization belongs to M-type

or noe from the spectral absorption characteristics of the sensitizing dye with respect to a silver halide adsorbing substrate which has been adjusted for a proper halogen composition by the use of, for example, Compound XI-(9) among compounds represented by the general formula (XI).

The present invention is advantageous in that  $S_{(\lambda)}$ , which is a factor of  $E_{(\lambda)}$ , is attributed to an M-type spectral sensitization, J-type spectral sensitization, or a spectral sensitization of a single structure such as inherent sensitivity of silver halide. Therefore, the gradation of images has a less fluctuation due to conditions of the object and printing conditions, and the gradation reproduction has a wide latitude. This is extremely advantageous to the present invention. On the other hand, the use of a J-type spectral sensitization leaves to be desired in that it is difficult for aggregates of a sensitizing dye to be removed

during the color development, causing color leaving and stain. Furthermore, the use of a J-type spectral sensitization is disadvantageous in that it tends to retard the progress of color development, particularly the progress of blix of reduced silver. Therefore, such a defect can be eliminated by an improvement in the development process.

A coloring material in which  $T_{(\lambda)}$  of the coloring material in a photographing color light-sensitive material is reflected by  $E_{(\lambda)}$ , particularly a magenta coloring material and a yellow coloring material is important in the present invention. Particularly, a coupler represented by the general formula (VIII) may by advantageously used in the present invention. Such a coupler is advantageous in that it facilitates the use of a masking coloring material for the longer wavelength side in a yellow coloring material or filter coloring material which is adapted to improve  $E_{(\lambda)}$  of GL in a color printing light-sensitive material. The use of such a coupler or a benzoylacetanilide type yellow coupler can provide a thin light-sensitive layer or improve image sharpness.

In a green sensitive layer (GL), the sensitizing dye may be selected from those represented by formula (III) to provide a maximum  $S(\lambda)$  given by a J-type spectral sensitization in order to make  $Eg(\lambda)$  independent from  $Eb(\lambda)$  or  $Er(\lambda)$ . Especially, it is preferred to carry out spectral sensitization so as to decrease a contribution by M-type spectral sensitization. For the purpose, a use of CR-compounds disclosed in Japanese Patent Application Nos. 311131/86 and 47225/87 is preferred.

The color printing light-sensitive material according to the present invention may be printed from a color print original, particularly from a color genative film or color slide, in the above described white color exposure process. A sharp band stop filter having a spectral absorption band in a wavelength band other than the range of  $\lambda_{smax} \pm 20$  nm,  $\lambda_{smax}$  being a wavelength of the maximum S( $\lambda$ ) of a light-sensitive layer of

a color printing light-sensitive material, may be preferably used in this exposure process. As a suitable sharp band stop filter there may be preferably used a band stop filter.

In the present invention, at least one of the color development bleach, fixing (or blix) and rinse and/or stabilization is effected in the presence of at least one of compounds represented by the general formula

(XI). Preferably, in the color development, at least one of the color developing solution, blix solution, bleaching solution, fixing solution, stabilizing bath, and rinsing bath may contain, as a fluorescent brightening agent or residual color remover, a compound represented by the general formula (XI) where X and Y preferably each represents -N =. Alternatively, the compound represented by the general formula (XI) may be incorporated in the light-sensitive material to be processed.

In the present invention, the pH value of the bleaching solution or blix solution is in the range of 3.5 to 6.0. The replenishing amount of the solution for the subsequent rinse and/or stabilization step may be 3 to 50 times the amount of the solution carried over from the pre-bath.

In the present invention, with a compound represented by the general formula (XI), a rapid development process for 20 seconds to 5 minutes can provide a color print surprisingly excellent in color reproducibility 45 without stain.

The compound represented by the general formula (XI) may be used as a supersensitizing dye for an M-type spectral sensitization process as described above.

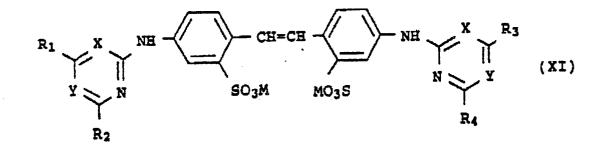
The compound represented by the general formula (XI) is advantageous in that it destroyes and puts H. D or J aggregates into a monomolecular adsorption state to intensify the M-type spectral sensitization, particularly when X and Y are not the same.

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wherein X and Y each represents = CH- or = N-;  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be the same or different and each represents a hydroxy group, halogen atom, heterocyclic amino group, heterocyclic thio group, alkoxy group, amino group, alkylamino group, aryloxy group or arylamino group; and M represents a monovalent cation, with the proviso that X and Y don't represent = CH- at the same time;

<sup>15</sup> Preferably, it is not the case that  $R_1$  and  $R_3$  are the same and  $R_2$  and  $R_4$  are the same at the same time, nor that  $R_1$  and  $R_4$  are the same and  $R_2$  and  $R_3$  are the same at the same time.

Preferably, X and Y each represents = N - at the same time. A compound represented by the general formula (I) wherein three or more sulfonic acid groups are incorporated in one molecule may be preferably used.

The incorporation of a specific fluorescent brightening agent defined by the general formula (XI) and an organic phosphonic chelating agent in the present color developing solution enables a remarkable elimination of fluctuation in photographic properties due to continuous processing.

A particularly remarkable effect of inhibiting stain or eliminating fluctuation in photographic properties can be observed particularly by using the compound represented by formula (XI) other than the compound of formula (XI) wherein  $R_1$  and  $R_3$  are the same and  $R_2$  and  $R_4$  are the same at the same time, or  $R_1$  and  $R_4$  are the same and  $R_2$  and  $R_4$  are the same at  $R_2$  and  $R_3$  are the same at the same time.

Such an effect becomes remarkable particularly when the light-sensitive material comprises particulate silver halide having a silver chloride content of 80 mot % or more. Furthermore, such an effect becomes remarkable particularly when the color developing solution to be used is substantially free of benzyl alcohol.

<sup>30</sup> Moreover, when the process following the color development (e.g. desilvering, rinse and stabilization) is short, and the replenishing amount of the solution to be used in the rinse or stabilization step is remarkably small, such an effect becomes remarkable. In accordance with the present invention, the amount of water and time which has been conventionally required to reduce mixture or residual color on a light-sensitive material is not necessarily needed.

The general formula (XI) will be further described hereinafter.

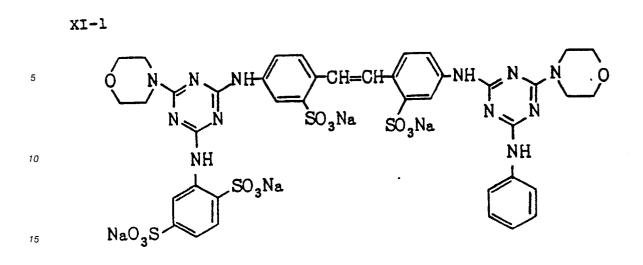
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each represents a hydroxy group,  $C_{1-4}$  alkoxy group such as methoxy group, ethoxy group, and methoxyethoxy group, amino group,  $C_{1-6}$  alkylamino group such as methylamino group, ethylamino group, propylamino group, dimethylamino group, cyclohexylamino group,  $\beta$ -hydroxyethylamino group, di( $\beta$ -hydroxyethyl)amino group,  $\beta$ -sulfoethylamino group, N-( $\beta$ -sulfoethyl)-N-methylamino group, and

<sup>40</sup>  $\beta$ -carboxyethyl group, aryloxy group such as phenoxy group, and p-sulfophenyl group, or arylamino group such as anilino group, o-, m-, and p-sulfoanilino group, o-, m- and p-chloroanilino group, o-, m- and ptoluidino group, o-, m- and p-carboxyanilino group, o-, m- and p-anisidino group, and o-, m- and phydroxyanilino group.

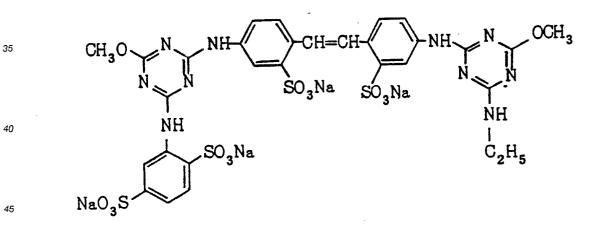
M represents a monovalent cation such as Na<sup>+</sup> and K<sup>+</sup>.

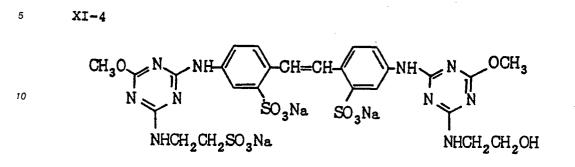
Specific examples of compounds of formula (XI) which can be used in the present invention will be shown hereinafter, but the present invention should be not construed as being limited thereto.

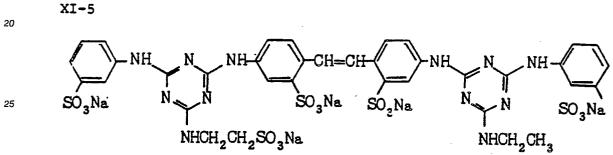
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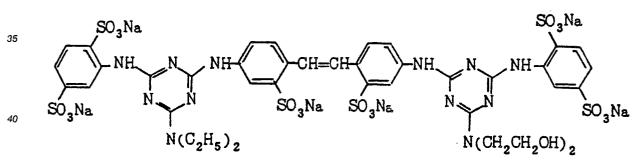
XI-3

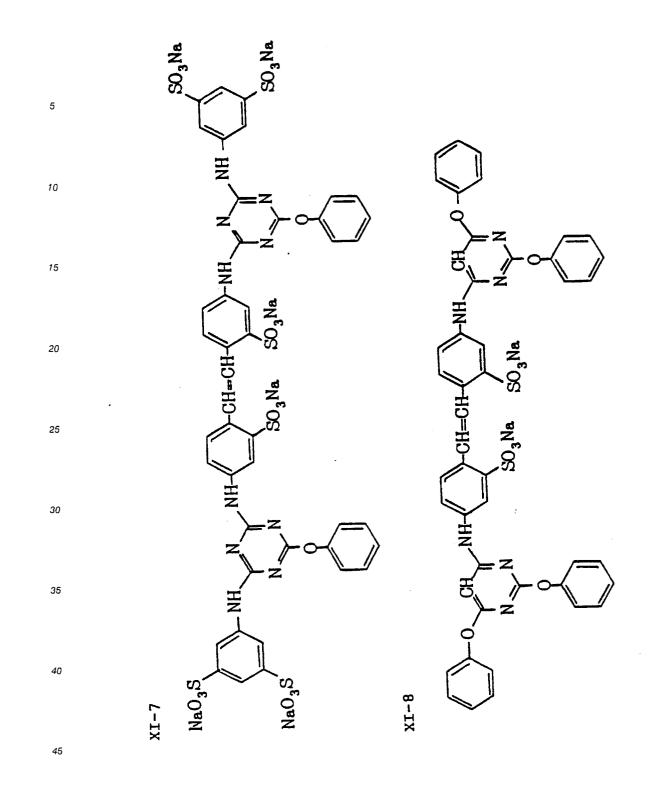






XI-6



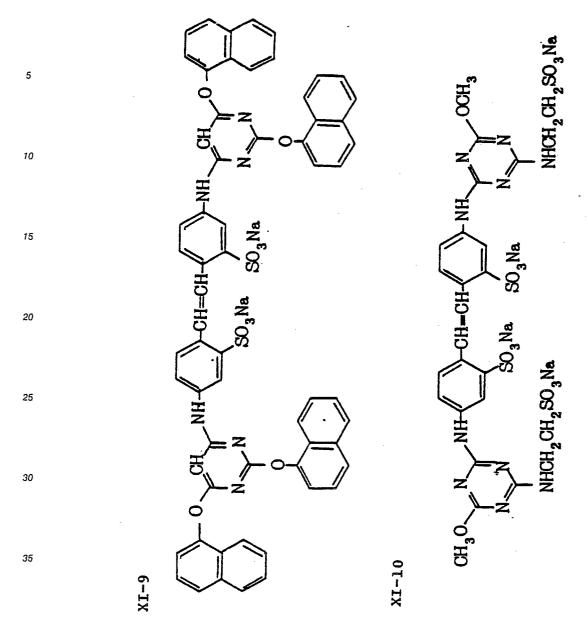


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The synthesis of a diaminostylene brightening agent which can be used in the present invention represented by formula (XI) can be accomplished by any suitable conventional method as described in Kaseihin Kogyokai, "Fluorescent Brightening Agent", August 1976, page 8.

The amount of such a fluorescent brightening agent to be added to a processing solution such as color 45 developing solution, blix solution and stabilizing solution is preferably in the range of 0.1 to 20 g/t, particularly 0.5 to 10 g/t.

The present silver halide emulsion particularly to be used in a color printing light-sensitive material is preferably a silver bromochloride emulsion substantially free of silver iodide and comprising silver chloride, silver bromide or mixed crystal thereof surrounded mainly by (100) plane as described in Japanese Patent

50 Application Nos. 39,825/87 and 319,741/87. The present silver halide emulsion is also preferably a silver bromochloride emulsion substantially free of silver iodide and comprising silver chloride, silver bromide or mixed crystal thereof surrounded mainly by (111) plane as described in Japanese Patent Application Nos. 47,225/87 and 150,320/87.

In the present invention, if the effect of the filter or filter layer is simultaneously used, silver bromide, silver bromochloride or silver chloride having various compositions can be used. In order to improve the color reproducibility according to the present invention, silver bromochloride having a silver bromide content of 30 mol% or less or silver bromochloride or silver chloride emulsion having a silver iodide content of 0.4 mol% or less and a silver bromide content of 10 mol% or less is preferably used.

In order to simultaneously provide rapidness in processing in a system according to the present technique, silver chloride having a silver bromide content of 3 mol% or less, preferably 1 mol% or less or substantially free of silver bromide is preferably used.

The incorporation of such a small amount of silver bromide not only gives an improvement in the rapidness of development but also is advantageous in that when a light-sensitive material containing such 5 an amount of silver iodide is continuously processed with a processing solution, bromide ions is a balanced accumulated amount determined by the relationship with the replenishing amount of the processing solution exists in the developing solution in a low concentration, making it possible to set the developing speed of the developing solution high itself.

The halogen composition of the silver halide emulsion to be used in the present invention influences 10 color leaving by dyes and desilvering during the color development. In particular, a high silver iodide content gives a disadvantageous effect.

The present silver halide emulsion contains silver iodide in a appropriate amount of 2 mol% or less, preferably 1 mol% or less, more preferably 0.4 mol%, most preferably none, based on the total amount of silver halide. The incorporation of silver iodide has many advantageous effects in light-sensitivity. In particular, silver iodide increases light absorption or spectral sensitizing dyes or inhibits desensitization due to a spectral sensitizing dye. However, if a system according to the present technique is subjected to a rapid development in a short period of time, a slow development speed causes a slow speed in development of the entire silver halide particles. This also gives a great disadvantages in the improvement of average color mixing degree in the present invention. The incorporation of silver iodide in an amount of 0.4 mol% or less may give an advantage in adsorption of spectral sensitizing dyes. However, it is preferred in the present invention to use a silver halide emulsion essentially free of silver iodide.

In a system according to the present technique, if a rapid development is required, silver chloride having a silver bromide content of 3 mol% or less, preferably 1 mol% or less or substantially free of silver bromide may be preferably used.

In order to obtain a light-sensitive material which is insusceptible to fog and exhibits a stable gradation in accordance with the present technique, it is desired to use an emulsion having a higher silver bromide content, e.g. 50 mol% or more. If the silver bromide content exceeds 95 mol%, the rapidness in development is slightly lowered. However, if a development accelerator such as 3-pyrazolidone, thioether and hydrazine is used with the emulsion, the rapidness in development can be recovered, making it possible to provide a high sensitivity light-sensitive material stable in preservability and proccessability.

Particulate silver halide to be contained in the present photographic emulsion may have a regular crystal structure such as cube, octahedron, and tetradecahedron, an irregular crystal structure such as sphere, and plate, a crystal structure having crystal defect such as twinning plane, or a composite thereof.

The preparation of a silver halide photographic emulsion which can be used in the present invention can be accomplished by any suitable method as described in Research Disclosure No. 17,643 (Dec. 1978, pp. 22-23, "I. Emulsion Preparation and Types"), Research Disclosure No. 18,716 (Nov. 1979, page 648). P. Glafkides, "Chemicet Phisque Photographique", Paul Montel, 1967, G. F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966, and V. L. Zelikman et al, "Making and Coating Photographic Emulsion", Focal Press, 1964.

Tabular particles having an aspect ratio of from about 2 or more, preferably about to about 10, more preferably about 5 to about 10 may be used in the present invention. Such tabular particles can be easily prepared by any suitable method as described in Gutoff, "Photographic Science and Engineering", as described in Gutoff, "Photographic Science and Engineering", Vol. 14, pp. 248-257, 1970, U.S. Patent Nos. 4,434,226, 4,414,310, 4,433,048, and 4,439,520, and British Patent No. 2,112,157.

The crystal structure of the present particulate silver halide may be uniform, or such that the halide composition varies between the inner portion and the outer portion thereof, or may be a layer. Alternatively, silver halides having different compositions may be connected to each other by an epitaxial junction or by any suitable compound other than silver halide such as silver thiocyanate, and zinc oxide.

Alternatively, a mixture of particles having various crystal structures may be used in the present invention.

The developability of particulate silver halide is determined not only by the halogen composition of the entire particles but also by the halogen distribution in the particles. Accordingly, the silver halide emulsion of the present invention preferably has some distribution or structure concerning the halogen composition in the particles thereof. A typical example of such a structure is a core/shell type or double structure type

55 particle in which the internal portion thereof differs from the surface thereof in halogen composition. In such a particle, the shape of the core may or may not be the same as that of the entire particle with the shell. In particular, both the core and the entire particle with the shell may be cubic, or the core may be octahedron

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while the entire particle with the shell may be cubic. Alternatively, the core may be in the form of a completely regular crystal while the entire particle with the shell may be slightly irregular. Furthermore, the particulate silver halide may not be merely double-structured but may be triple-structured or may have a higher multistructure. Moreover, the surface of a core/shell double-structured particle may be provided with ag thin film of silver halide having a different halogen composition.

- Preferable silver halide particles have maldistributed phases comprising layer structure or discontinuous isolated structure containing a different halide distribution on a surface or internal part of particles from in other phases. Preferably silver chlorobromide particles having maldistributed phases have a cubic structure having (100) plane or tetradecahedron, and also have a structure of octahedron having (111) plane or tabular particles, especially having 2 to 10 of aspect ratio. 10
  - An emulsion containing particulate silver halide which has been adjusted for proper development starting points as described in Japanese Patent Application Nos. 319,741/87, 323,214/87 and 150,320/87 may be particularly preferably used in the present invention. CR-compound as described in the above cited specification may be preferably sensitizing dyes.
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The average size of particles to be used in the present silver halide emulsion is preferably in the range of 0.1 to 2 µm, particularly 0.15 to 1.4 µm as calculated in terms of diameter of sphere having the same volume.

The particle size distribution of the present particulate silver halide is preferably narrow. A monodisperse emulsion is preferably used in the present invention. In particular, a monodisperse emulsion of

- particles having a regular crystal shape may be preferably used in the present invention. An emulsion of 20 silver halide particles, preferably 90% or more, more preferably 95% or more by weight or number of particles of which fall within ±20% of the average particle size may be preferably used in the present invention. Monodisperse emulsion is preferred as is disclosed in U.S. Patents 3,574,628 and 3,655,394, and Great Britain Patent 1,413,748, etc. In the case of such a monodisperse emulsion, an emulsion comprising
- particulate silver halide having any suitable construction as described above may be preferably used in the 25 present invention. Two or more different kinds of monodisperse emulsions of cubic or tetradecahedron particulate silver halide may be used in admixture or by coating in multilayer to provide an excellent result. If two or more kinds of monodisperse emulsions are used in admixture, the mixing ratio as calculated in terms of amount of silver is preferably 5 to 95%. The ratio of average particle size of emulsion particles to
- be mixed is 1:1.1 to 1:8, preferably 1:1.2 to 1:6 as calculated in terms of volume. When two kinds of 30 monodisperse emulsions are used in admixture, the mixing ratio is calculated in terms of amount of silver is preferably in the range of 0.05:0.95 to 0.95:0.05, particularly 0.1:0.9 to 0:9:0.1.

The preparation of a silver bromochloride emulsion to be used in the present invention can be accomplished by any one of acidic process, neutral process, and ammonia process. Particularly preferred among these processes is acidic process. The process for the reaction of the soluble silver salt with the 35 soluble silver halide can be accomplished by separate mixing process, simultaneous mixing process, or combination thereof. In order to obtain monodisperse particles of the present invention, simultaneous mixing process may be preferably used. The process for the reaction of the soluble silver salt with the soluble

- silver halide can be also accomplished by a process in which particles are formed in excess silver ions (socalled reversal mixing process). One form of the simultaneous mixing process is a so-called controlled 40 double jet-process in which the pAg of the liquid phase in which silver halide is formed is kept constant. This process can provide a silver halide emulsion suitable for the present invention having a regular crystal structure and a narrow particle size distribution. Such particles which can be preferably used in the present invention may be preferably prepared on the basis of the simultaneous mixing process.
- In the process of formation or physical ripening of particulate silver halide, cadmium salt, zinc salt, lead 45 salt, thallium salt, iridium salt, or complex salt thereof, rhodium salt or complex thereof, or iron salt or complex salt thereof may be present.

In particular, iridium salt or complex salt thereof may be used in an amount of  $10^{-9}$  to  $10^{-4}$  mol/mol, preferably 10<sup>-8</sup> to 10-5 mol/mol. As compared to an emulsion which has been prepared without using an iridium salt or complex salt thereof, such a consideration is useful particularly when a rapid developability or stability is desired for a light-sensitive material which has been subjected to high intensity or low intensity

If physical ripening is effected in the presence of any known silver halide solvent such as ammonia, potassium thiocyanate, and thioether or thione as described in U.S. Patent No. 3,271,157, and Japanese Patent Application (OPI) Nos. 12,360/76, 82,408/78, 114/319/78, 100,717/79, a monodisperse emulsion of 55 particulate silver halide having a regular crystal structure and a narrow particle size distribution can be advantageously obtained.

exposure out of the proper exposure intensity range.

The removal of the soluble silver salts from the emulsion which has been subjected to physical ripening

can be accomplished by any suitable method such as noodle rinsing process, flocculation sedimentation process, and ultrafiltration process.

The silver halide emulsion to be used in the present invention can be subjected to chemical sensitization such as selenium sensitization, reduction sensitization, noble metal sensitization, or combination thereof. In particular, sulfur sensitization process using active gelatin or sulfur-containing compound capable of reacting with silver ion such as thiosulfate, thiourea compound, mercapto compound, and rhodanine compound, reduction sensitization process using a reducing substance such as stannous salt, amine salt, hydrazine derivative, formamidinesulfinic acid, and silane compound, and noble metal sensitization process using a metal compound such as gold complex, and complex salt of the group VIII metals such

10 as Pt, Ir, Pd, Rh, and Fe can be used singly or in combination. The present monodisperse silver bromochloride emulsion may be preferably subjected to sulfur sensitization or selenium sensitization. Such a senisitization process may be preferably effected in the presence of a hydroxylazaindene compound.

Preferred examples of a silver halide emulsion to be incorporated in the direct positive color printing light-sensitive material include an emulsion of internal latent type silver halide particles having the above described halogen composition and a multilayer construction as described in Japanese Patent Application Nos. 25,737'87.

Preferred examples of a silver halide emulsion to be incorporated in the color reversal printing lightsensitive material include those described in European Patent No. 0217353A-2, and Japanese Patent Application (OPI) Nos. 39,043/86, and 61,156/86.

The blue-sensitive layer in the color printing light-sensitive material may preferably comprise a sensitizing dye such that it is not strongly sensitized to a long wavelength up to about 485 nm and is given a high spectral sensitivity in a shorter wavelength band less than about 485 nm, more preferalby less than about 460 nm, depending on the spectral absorption characterisitcs of dyes to be used in the color print original. In particular, the silver halide may be preferably subjected to a spectral sensitization such that the

inherent sensitivity thereof is limited in a short wavelength band and it is strongly sensitized on the long wavelength side, e.g., 450 to 470 nm while its sensitization is cut in a longer wavelength band, e.g., 485 nm or more.

In the coupler to be used in the present invention, the spectral absorption by a dye obtained by the coupling reaction of the respective yellow, magenta and cyan coupler in a color light-sensitive material for

<sup>30</sup> use in photographing with a color developing agent may preferably correspond to the spectral absorption by the corresponding blue-sensitive layer, green-sensitive layer or red-sensitive layer in a color printing light-sensitive material, and there is substantially no spectral absorption in the range of wavelength of spectral sensitivity of light-sensitive layers other than the corresponding light-sensitive layer. Furthermore, the spectral absorption by a dye obtained in a color light-sensitive material for use in photographing is

- preferably out of the range of  $\lambda E_{max} \pm 20$  nm,  $\lambda E_{max}$  being the maximum spectral light amount of lightsensitive layers other than the corresponding light-sensitive layer of a color printing light-sensitive, preferably out of the range of  $\lambda E_{max} \pm 30$  nm. For example, when the spectral absorption of a magenta dye image obtained in a color negative film is out of the main spectral sensitivity wavelength range of lightsensitive layers other than the corresponding green-sensitive layer in a color paper, i.e., about 400 to 485
- 40 nm for blue-sensitive layer or 600 to 740 nm for red-sensitive layer, the present invention gives an unprecedentely remarkable improvement in color reproducibility. This is because that the disadvantageous effects by the spectral absorption by a dye in a cut wavelength range given by the present band cut filter is substantially completely eliminated.

Preferably, the spectral absorption by a yellow, magenta or cyan dye obtained from a coupler to be used in a color printing light-sensitive material is only seen in the wavelength range of spectral absorption by a blue-sensitive layer, green-sensitive layer or red-sensitive layer in a color light-sensitive material for use in photographing. Couplers which may be generally used in the present invention are described in patents cited in Research Disclosure No. 17,643, VII-C to G.

As suitable yellow couplers there can be used those described in U.S. Patent Nos. 3,933,501, 50 4,022,620, 4,326,024, and 4,401,752, Japanese Patent Publication No. 10,739/83, and British Patent Nos. 1,425,020, and 1,476,760.

As suitable magenta couplers there may be used 5-pyrazolone and pyrazoloazole compounds. Particularly preferred examples of such magenta couplers are described in U.S. Patent Nos. 4,310,619, 4,351,897, 3,061,432, 3,725,067, 4,500,630, and 4,540,654, European Patent No. 73,636, Research Disclosure Nos. 24,220 (June 1984) and 24,230 (June 1984), and Japanese Patent Application (OPI) Nos. 33,552/85, and 43,659/85.

As suitable cyan couplers there may be used phenolic and naphtholic couplers. Preferred examples of such couplers are described in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929,

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2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, 4,327,173, 3,446,622, 4,333,999, 4,451,559, and 4,427,767, West German Patent Disclosure No. 3,329,729, and European Patent Nos. 121,365A, and 161,626A.

As colored couplers for correcting undesired absorption by color forming dye there may be used those described in Research Disclosure No. 17,643 (VII-G), U.S. Patent Nos. 4,163,670, 4,004,929, and 4,138,258, Japanese Patent Publication No. 39,413,82, and British Patent No. 1,146,368.

As suitable couplers which form a colored dye having a proper diffusibility there may be used those described in U.S. Patent No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570, and West German Patent (Disclosure) No. 3,234,533.

Typical examples of polymerized dye-forming coupler couplers are described in U.S. Patent Nos. 3,451,820, 4,080,211, and 4,367,282, and British Patent No. 2,102,173.

Couplers which release a photographically useful residual group upon coupling can be preferably used in the present invention. As DIR couplers which release a development inhibitor there can be preferably used those described in patents cited in Research Disclosure No. 17,643 (VII-F), Japanese Patent Application (OPI) Nos. 151,944.82, 154,234.82, and 184,248/85, and U.S. Patent No. 4,248,962.

As couplers which imagewise release a nucleating agent or development accelerator upon development there can be used those described in British Patent Nos. 2,097,140, and 2,131,188, and Japanese Patent Application (OPI) Nos. 157,638.84, and 170,840/84.

Other examples of couplers which can be incorporated in the present light-sensitive material include competitive couplers as described in U.S. Patent No. 4,130,427, poly-equivalent couplers as described in U.S. Patent Nos. 4,283,472, 4,338,393, and 4,310,618, DIR redox compound-releasing couplers as described in Japanese Patent Application (OPI) No. 185,950/85, and couplers which release a dye which recovers its original color after being separated as described in European Patent No. 173,302A.

Useful examples of couplers which can be used in a color printing light-sensitive material which accomplishes the effects of the present invention include magenta couplers as described in European Patent 226,849 A, cyan couplers as described in Japanese Patent Application (OPI) No. 105,229/83, and color couplers as described in Japanese Patent Application No. 39,825/87. Particularly preferred examples of such couplers inlcude color couplers represented by the general formulas (VII-a), (VII-b), (VIII), (IX) and (X).

R72. 1 NHCOR71

$$R_{73} \xrightarrow{V_1} V_1 \qquad (VII-a)$$

$$R_{74} \xrightarrow{O} H \\ N H C O R_{74} \qquad (VII-b)$$

$$R_{75} C O N H \\ Y_2$$

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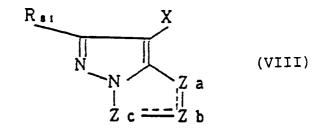
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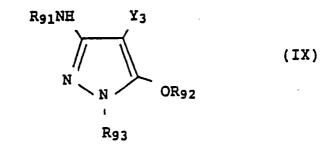
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wherein R<sub>71</sub>, R<sub>74</sub>, and R<sub>75</sub> each represents an aliphatic group (the term "aliphatic group" as used herein means a straight-chain, branched or cyclic alkyl, alkenyl or alkynyl group), aromatic group, heterocyclic group, aliphatic amino group, aromatic amino group or heterocyclic amino group; R<sub>73</sub> represents an aliphatic group; R<sub>72</sub> and R<sub>76</sub> each represents a hydrogen atom, halogen atom, aliphatic group, aliphatic oxy group, or acylamino group; and Y<sub>1</sub> and Y<sub>2</sub> each represents a hydrogen atom or group which can be separated after coupling reaction with an oxidation product of a color developing agent (hereinafter including an atom, such as a halogen atom), with the proviso that R<sub>72</sub> and R<sub>73</sub> or R<sub>75</sub> and R<sub>76</sub> may be connected to each other to form 5-, 6- or 7-membered condensated carbostyryl or oxyindole ring, R<sub>72</sub> and R<sub>73</sub> may be

condensated to form a substituted naphthol ring, and R<sub>71</sub>, R<sub>72</sub>, R<sub>73</sub> or Y<sub>1</sub>, or R<sub>74</sub>, R<sub>75</sub>, R<sub>75</sub> or Y<sub>2</sub> may together form a dimer or higher polymer.



In general formula (VIII), R<sub>81</sub> represents a hydrogen atom or substituent. Preferred examples of such a substituent include alkyl group such as methyl group, ethyl group, and butyl group; branched alkyl group 15 such as isopropyl group, isobutyl group, and tertiary butyl group; substituted alkyl group (including branched groups); alkoxy group such as methoxy group, ethoxy group, and butoxy group; substituted alkoxy group such as ethoxyethoxy group, and phenoxyethoxy group, o-methoxyphenoxyethoxy group, obutoxyphenoxyethoxy group, o-chlorophenoxyethoxy group; aryloxy group such as phenoxy group, omethoxyphenoxy group, o-butoxyphenoxy group, o-chlorophenoxy group; and ureide group. Particularly 20 preferred among these groups are branched alkyl group and substituted or unsubstituted alkoxy group. X represents a hydrogen atom or group which can be separated upon a coupling reaction with an oxidation product of an aromatic primary amine color developing agent. Examples of such a group include halogen atom such as chlorine atom and bromine atom, arylthio group such as 2-butoxy-5-t-octylphenylthio group, and 2-propoxy-5-t-hexyphenylthio group, nitrogen-containing heterocyclic group such as imidazole group, 25 and 4-chloroimidazole group, and aryloxy group such as p-methylphenoxy group, 2,4-dimethylphenoxy group, and 2,4-dimethyl-t-phenoxy group. Particularly preferred among these groups are halogen atom and arylthio group. Za, Zb and Zc each represents a methine, substituted methine, or = N-NH-. One of Za-Zb bond and Zb-Zc bond is a double bond, and the other is a single bond. If Za-Zb is a carbon-carbon double bond, it may be a part of an aromatic ring. Furthermore, R<sub>81</sub> or X may form a dimer or higher polymer. If 30 Za, Zb or Za is a substituted methine, the substituted methine may form a dimer or higher polymer. When Za, Zb or Zc represents a substituted methine, the substituent is preferably a substituted alkyl group, particularly a branched substituted alkyl group such as substituted isopropyl group, and substituted tertiary butyl group. As a substituent for a substituted methine group, an aryl group such as a halogen substituted phenyl group is also preferable.



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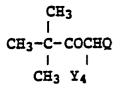
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wherein  $Y_3$  represents a hydrogen atom or coupling-off group;  $R_{91}$  and  $R_{93}$  each represents a substituted or unsubstituted phenyl group; and  $R_{92}$  represents a hydrogen atom; aliphatic group or aromatic acyl or sulfonyl group. Preferable  $Y_3$  is a hydrogen atom or a coupling-off group containing sulfur atom as a coupling-off atom. Preferable  $R_{91}$  group is a substituted phenyl group and preferable  $R_{93}$  group is a trichlorophenyl group.

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(X)

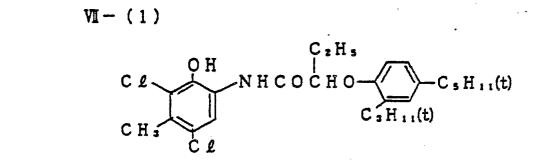
wherein Q represents a substituted or unsubstituted N-phenylcarbamoyl group; and Y<sub>4</sub> represents a halogen atom or the other group capable of released upon a coupling reaction with an oxidation product of a developing agent (preferable coupling-off atom contained in the coupling-off group is a nitrogen atom).

The couplers to be used in the present invention may be incorporated in a light-sensitive material by various known dispersion processes.

Examples of high boiling solvents to be used in an oil-in-water dispersion process are described in U.S. Patent 2,322,027.

Specific examples of procedure and effects of latex dispersion process and latex to be used in impregnation are described in U.S. Patent No. 4,199,363, and West German Patent Application (OLS) Nos. 2,541,274, and 2,541,230.

Specific examples of main couplers for the formation of dye which can be incorporated in a color lightsensitive material for use in photographing or color printing light-sensitive material will be shown hereinafter.



$$\mathbf{VI} = (2)$$

<sup>35</sup> <sup>40</sup> (t) C<sub>s</sub> H<sub>11</sub>  $\longrightarrow$  O - C H C N H C - C  $\ell$  C  $\ell$ 

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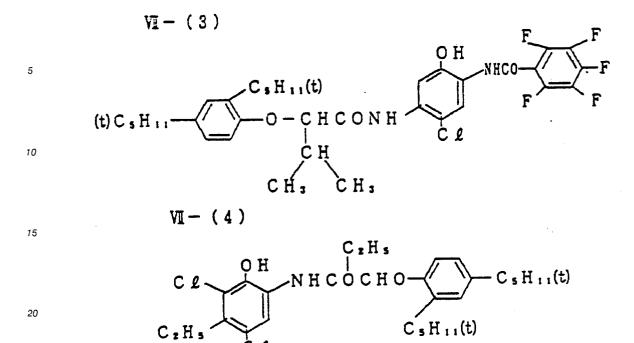
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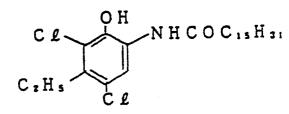
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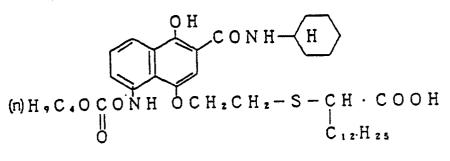


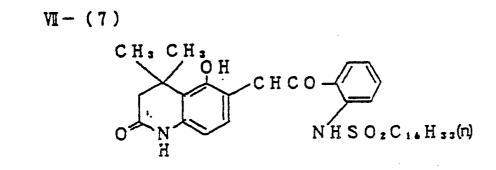
VI- (5)



VI - (6)

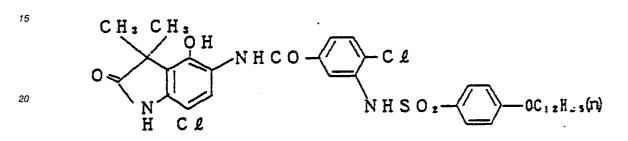
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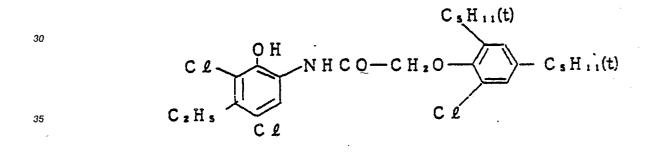


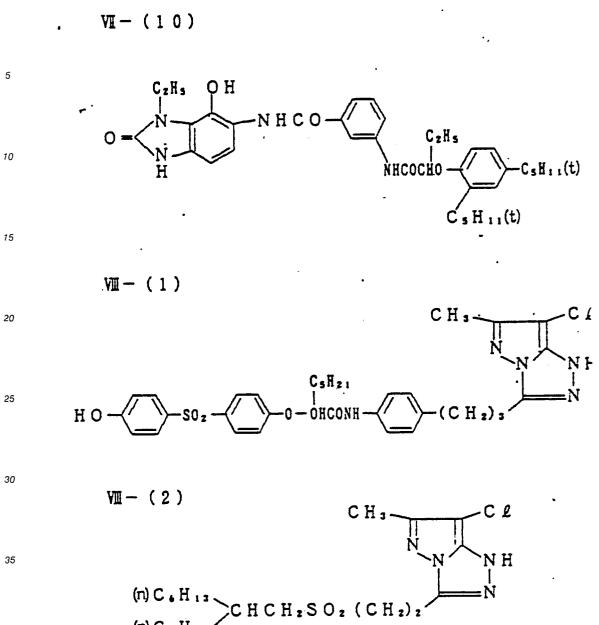
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VI- (8)

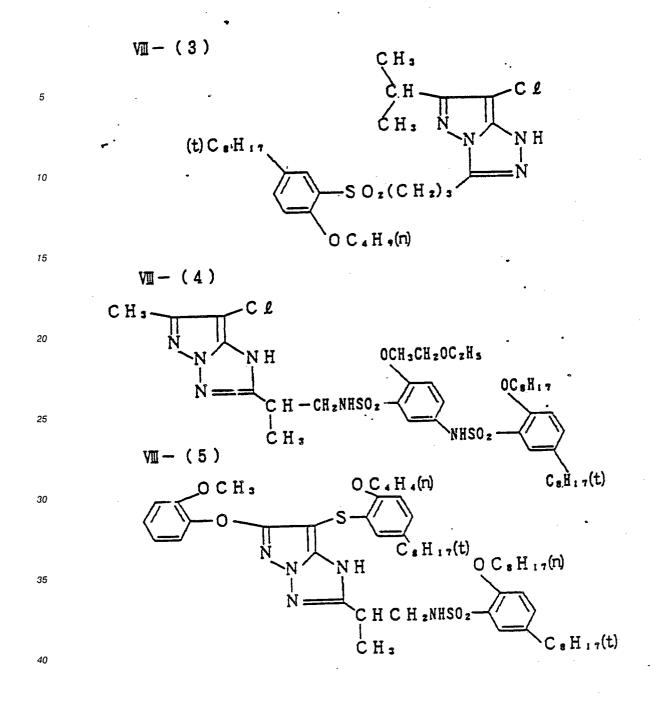


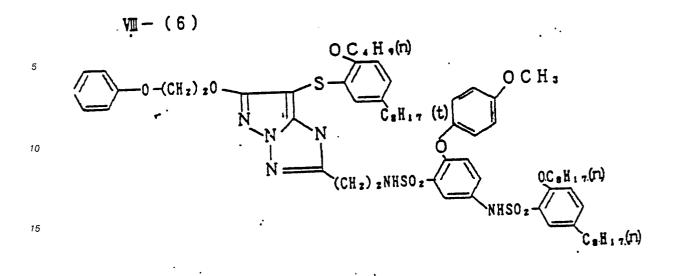
VI- (9)

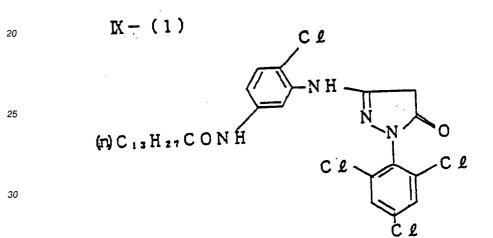




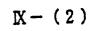
(n) C • H 13 (n) C • H 17

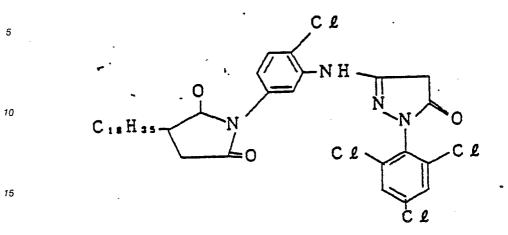




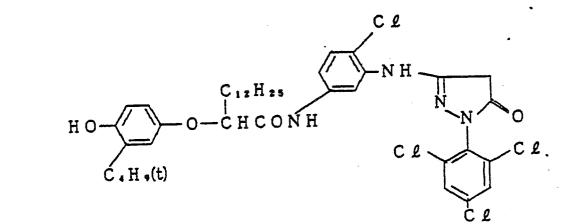


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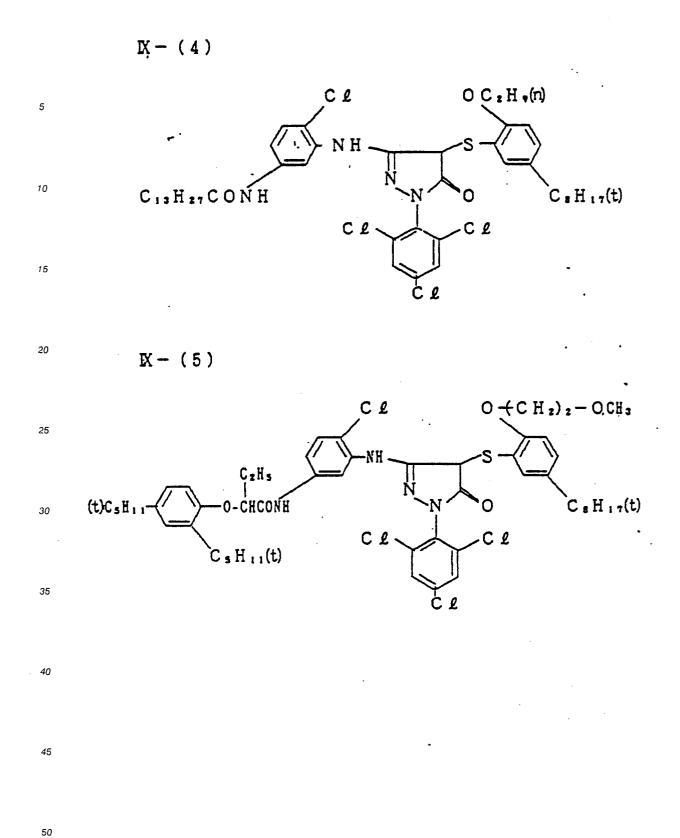


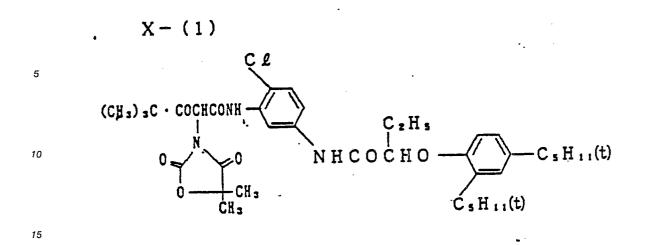


X-(3)



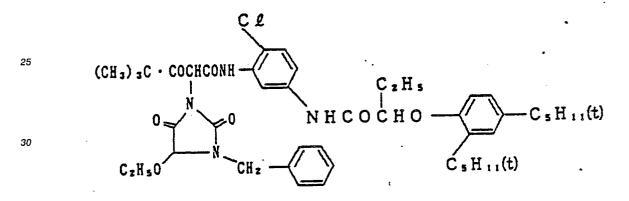
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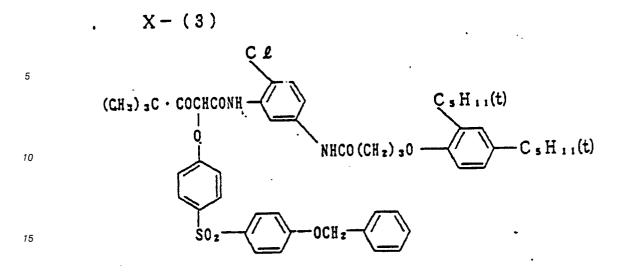




X-(2)

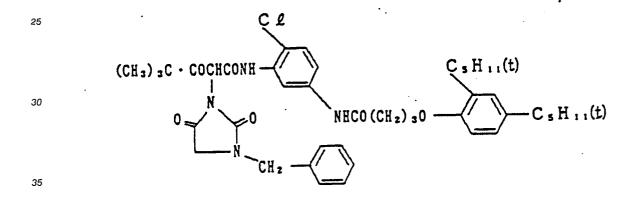


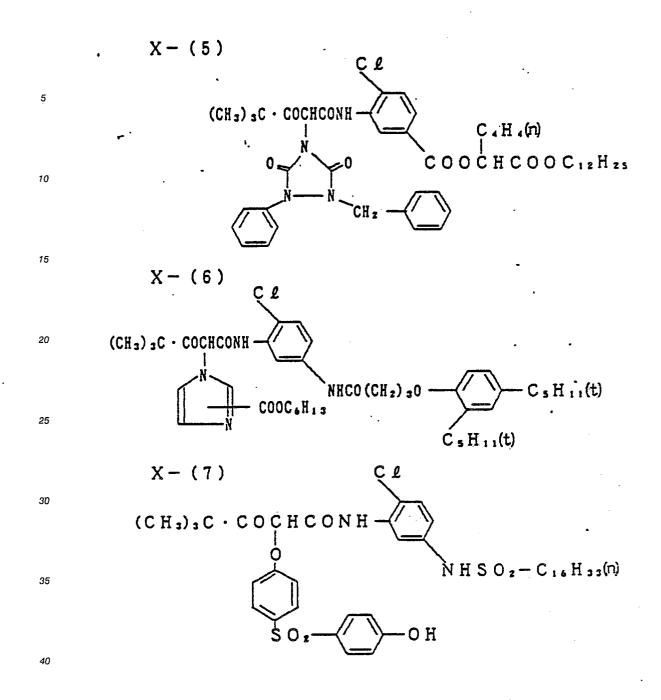


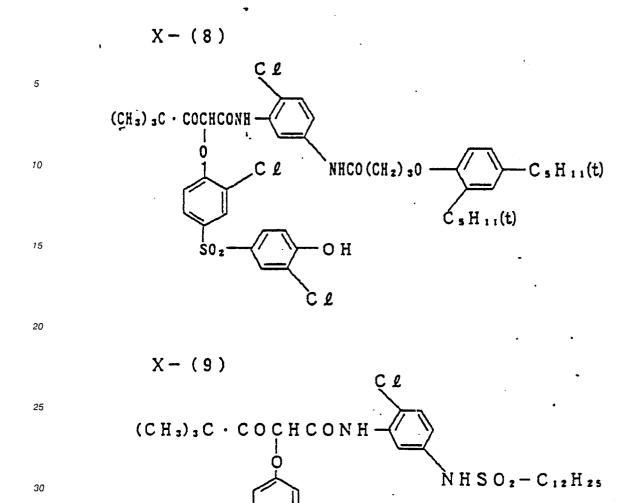


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X-(4)







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Examples of known photographic additives which may be used in the present invention are described in Research Disclosure Nos. 17,643 and 18,716. The places where such a description is found are summarized in the table below.

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5		Additives ·	RD 17643	RD 18716
	1.	Chemical sensitizer	Page 23	Right column on
				page 648
10	2.	Sensitivity improver		8
	3.	Spectral sensitizer,	pp, 23 - 24	Right column on
15		supe. ensitizer	•	page 648 - right
15		•		column on page 649
	4.	Brightening agent	Page 24	
20	5.	Fog inhibitor,	pp. 24 - 25	Right column on
		stabilizer	• •	page 649
	6.	Light absorber, filter	pp. 25 - 26	Right column on
25		dye, ultraviolet	N	page 649 - left
-		absorber	·. ·.	column on page
				650
30	7.	Stain inhibitor	Right column on	Left column to
			page 25 -	right column on
35			•	page 650
	. 8.	Dye stabilizer	Page 25	
	9.	Film hardener	Page 26	Left column on
40			·.	page 651
	10.	Binder	Page 26	<b>PI</b> .
45		•		
		11. Plasticizer, lubrica	ant Page 27	Right column
50				on page 650
50		12. Coating aid, surface	e pp. 26 - 27	87
		active agent		
		13. Antistatic agent	Page 27	ite.

Examples of suitable supports which can be used in the present invention are described on page 28 of Research Disclosure No. 17,643 and from the right column on page 647 to the left column on page 648 in

Research Disclosure No, 18,716.

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The printed color printing light-sensitive material according to the present invention may be preferably subjected to color development, blix, rinse and/or stabilization. Typical examples of processing steps will be described hereinafter, but the present invention should not be construed as being limited thereto. The term "blix" as used herein means a so-called blix in which bleaching and fixing are simultaneously proceeded or a process in which bleaching and fixing are separately .proceeded

1. Color development - blix -

10	rinse
	2. Color development - blix -
15	rinse
20	stabilization 3. Color development - bleaching - blix -
25	4. Color development - bleaching - blix -
30	Stabilization 5. Color development - rinse - blix -
35	6. Color development - fixing - blix -
40	stabilization 7. Black-and-white development - rinse - color development - blix -
45	rinse
50	8. Black-and-white development rinse - color development - rinse - blix
	The above described
55	rinse

step may be replaced by the stabilizing step. The supply amount of the processing solution is 3 to 50 times

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the amount of the processing solution carried over from the pre-bath.

In recent years, as the time for processing of a color printing light-sensitive material has been shortened, and the time for continuous processing has been prolonged, the color printing light-sensitive material according to the present invention may be susceptible to dye leaving, poor desilvering, and stain.

- 5 The color developing solution to be used in the present invention may comprise any suitable known aromatic primary amine color developing agent. A preferred example of such an aromatic primary amine color developing agent is a p-phenylenediamine derivative. Typical examples of such a p-phenylenediamine derivative will be shown hereinafter, but the present invention should not be construed as being limited thereto.
- 10 D-1: N.N-diethyl-p-phenylenediamine

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D-2: 2-Amino-5-diethylaminotoluene

D-3: 2-Amino-5-(N-ethyl-N-laurylamino)toluene

- D-4: 4-[N-ethyl-N-(β-hydroxyethyl)amino]aniline
- D-5: 2-Methyl-4-[N-ethyl-N-[
  \$-hydroxyethyl)amino]aniline
- D-6: 4-Amino-3-methyl-N-ethyl-N-[ß-(methanesulfonamide)ethyl]aniline
- D-7: N-(2-amino-5-diethylaminophenylethyl)meth. anesulfonamide
- D-8: N,N-dimethyl-p-phenylenediamine
- D-9: 4-Amino-3-methyl-N-ethyl-N-methoxyethylaniline
- D-10: 4-Amino-3-methyl-N-ethyl-N-*β*-ethoxyethylaniline
- D-11: 4-Amino-3-methyl-N-ethyl-N-β-butoxyethylaniline

Particularly preferred among these p-phenylenediamine derivatives is 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamide)ethyl]-aniline (exemplary compound D-6).

These p-phenylenediamine derivatives may be salts such as sulfates, hydrochloride, sulfites, and ptoluenesulfonates. The amount of such an aromatic primary amine developing agent to be used is preferably in the range of about 0.1 to about 20 g, particularly about 0.5 to about 10 g per 1 t of developing solution.

The present color developing solution may optionally comprise any suitable development accelerator. However, the present color developing solution preferably doesn't contain benzyl alcohol in the light of pollution, facility in solution preparation, and fog inhibition. In particular, the present color developing solution may contain benzyl alcohol in an amount of 5 ml or less, preferably 2 ml or less per 1 t thereof.

Preferably, the present color developing solution is free of benzyl alcohol.

The present color developing solution may optionally comprise any other preservatives such as sulfite, e.g., sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, and potassium methasulfite, and carbonyl-sulfite addition product. The added amount of such a preservative is in the range of 0 to 20 g/t, preferably 0 to 5 g/t. If the preservability of the color developing solution thus

- prepared can be fully attained, the added amount of such a preservative is preferably less. If the color developing solution contains a small amount of sulfite ion, the colour developing capability thereof can be improved without increasing the used amount of silver halide or color couplers. On the other hand, it is known that the reduction in the sulfite ion content increases color stain and deteriorates color
- 40 reproducibility. However, the present color image formation process using compounds represented by formula (XI) enables a processing which causes less color stain and provides an excellent color developing capability.

Sulfite ion may serve as a solvent for a silver halide emulsion having a high chlorine content (high silver chloride content emulsion), causing a remarkable reduction in the concentration of sulfite ion. If the sulfite

45. ion concentration in the color developing solution varies due to the above described effect, the photographic properties, particularly printer conditions in the case of a printing light-sensitive material, show a continuous change.

In the present invention, the substantial absence of sulfite ion may be preferably compensated by the incorporation of an organic preservative as described hereinafter.

<sup>50</sup> In other words, the incorporation of such an organic preservative can stabilize the color developing solution and improve color mixture inhibition without deteriorating the color developing capability.

An organic preservative can be used in the present invention is an organic compound which reduces the speed of deterioration of an aromatic primary amine color developing agent when incorporated in a solution for the processing of a color photographic light-sensitive material. In other words, such an organic

compound serves to inhibit oxidation of a color developing agent by air. Particularly useful examples of such an organic preservative include hydroxylamines, hydroxams, hydrazines, hydrazides, phenols, α hydroxyketones, α-aminoketones, saccharides, monoamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and condensed ring amines.

## EP 0 295 716 A2

As compounds for directly preserving the above described color developing agent there may be preferably used various hydroxylamines, hydroxamic acids as described in Japanese Patent Application No. 186,559,86, hydrazines and hydrazides as described in Japanese Patent Application No. 186,559,86, hydrazines and hydrazides as described in Japanese Patent Application No. 170,756/86, phenols as described in Japanese Patent Application No. 188,742/86, and 203,253/86,  $\alpha$ -hydroxyketones and  $\alpha$ -aminoketones as described in Japanese Patent Application No. 188,742/86, and 203,253/86,  $\alpha$ -hydroxyketones and  $\alpha$ -aminoketones as described in Japanese Patent Application No. 180,616/86. Examples of Compounds which can be used in combination with these compounds include monoamines as described in Japanese Patent Application Nos. 147,823,86, 166,674/86, 165,621,86, 164,515/86, 170,789/86, and 168,159/86, diamines as described in

- Japanese Patent Application Nos. 173,595/86, 164,515/86, and 186,560/86, polyamines as described in Japanese Patent Application Nos. 165,621 86, 169,789/86, and 188,619/86, nitroxy radicals as described in Japanese Patent Application No. 197,760/86, alcohols as described in Japanese Patent Application Nos. 186,561 86, and 197,419/86, oxims as described in Japanese Patent Application No. 198,987/86, and tertiary amines as described in Japanese Patent Application No. 265,149/86. The present color developing
- 15 solution may also contain an agent for restoring or capturing oxidation product of color developing agent as described in Japanese Patent Application No. 259,799/86. Other examples of preservatives which may be optionally incorporated in the present color developing solution include various metals as described in Japanese Patent Application (OPI) Nos. 44,148/82, and 53,749/82, salicylic acids as described in Japanese Patent Application (OPI) No. 180,588/84, alkanolamines as described in Japanese Patent Application (OPI) No. 180,588/84, alkanolamines as described in Japanese Patent Application (OPI) No. 3,532/79 and Japanese Patent Publication 57,586/85, polyethyleneimines as described in Japanese

Patent Application (OPI) No. 94,349/81, and aromatic polyhydroxy compounds as described in U.S. Patent No. 3,746,544. Particularly preferred among these compounds are aromatic polyhydroxy compounds.

The color developing solution to be used in the present invention preferably has a pH value of 9 to 12, particularly 9 to 11.0. The present color developing solution may contain compounds which constitute known developing solutions.

In order to maintain the above specified pH value, various buffering agents may be preferably used. As such buffering agents there may be used carbonates, phosphates, borates, tetraborates, hydroxybenzoates, glycine salts, N,N-dimethylglycine salts, leucine salts, norleucine salts, guanine salts, 3,4-dihydroxyphenylalanine salts, alanine salts, aminobutyrates, 2-amino-2-methyl-1,3-propanediolates, valine salts, proline salts,

30 trishydroxyaminomethane salts, or lysine salts. Particularly, carbonates, phosphates, tetraborates, and hydroxybenzoates are excellent in solubility and buffering action at a high pH range of 9.0 or more. When these salts are added to a color developing solution, they don't exert any bad influence upon photographic properties, e.g., fog inhibition. These salts are inexpensive. In the light of such advantages, these salts may be particularly preferably used.

The amount of such a buffering agent to be incorporated in the color developing solution is preferably in the range of 0.1 mol/ or more, particularly 0.1 to 0.4 mol/.

In the present invention, an organic phosphoric compound as described in Japanese Patent Application No. 37,350/87 may be preferably used. The added amount of such an organic phosphonic compound is in the range of 0.1 to 40 g, preferably 0.2 to 10 g per l of color developing solution.

The present color developing solution may also contain various chelating agents other than organic phosphonic chelating agents.

Specific examples of chelating agents which can be used in combination with other additives include nitrilotriacetic acid, diethylenetriaminepentaacetic acid, ethylenediamine tetraacetic acid, trancyclohexanediaminetetra-acetic acid, 1,2-diaminopropanetetraacetic acid, 1,2-diaminop

as being limited to these chelating agents.

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These chelating agents may optionally be used in combination.

The present color developing solution may optionally comprise any suitable development accelerator. However, the present color developing solution may preferably be substantially free of benzyl alcohol in the light of pollution, facility in solution preparation, fog inhibition, and stain inhibition.

Other examples of development accelerators which can be optionally incorporated in the present color developing solution include thioether compounds as described in Japanese Patent Publication Nos. 16,088/62, 5,987/72, 7,826/63, 12,380/69, and 9,019/70, p-phenylenediamine compounds as described in

<sup>55</sup> Japanese Patent Application (OPI) Nos. 49,829/77, and 15,554/75, quaternary ammonium salts as described in Japanese Patent Application (OPI) Nos. 49,829/77, and 15,554/75, quaternary ammonium salts as described in Japanese Patent Application (OPI) Nos. 137,726/75, 156,826/81, and 43,429/77, and Japanese Patent Publication No. 30,074/69, amine compounds as described in U.S. Patent Nos. 2,494,903, 3,128,182, 4,230,796, 3,253,919, 2,482,546, 2,596,926, and 3,582,346, and Japanese Patent Publication No. 11,431/66, and polyalkylene oxides as described in Japanese Patent Publication Nos. 16,088/62, 25,201/67, 11,431/66, and 23,883/67, and U.S. Patent 3,128,183, and 3,532,501, 1-phenyl-3-pyrazolidones, and imidazoles.

- In the present invention, any suitable fog inhibitor may be optionally used. As such a fog inhibitor there may be used a halide of an alkaline metal such as sodium chloride, potassium bromide, and potassium iodide, or an organic fog inhibitor. Typical examples of such an organic fog inhibitor include nitrogencontaining heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolylbenzimidazole, 2thiazolylmethyl-benzimidazole, indazole, hydroxyazaindolidine, and adenine.
- The present color developing solution may optionally contain various active agents such as alkylsulfonic acid, arylphosphonic acid, aliphatic carboxylic acid, and aromatic carboxylic acid.

The temperature at which the present color developing solution is used is in the range of 20 to 50°C, preferably 30 to 40°C. The processinhg time is in the range of 20 seconds to 5 minutes, preferably 30 seconds to 2 minutes. The replenishing amount of the present color developing solution is preferably less

<sup>15</sup> and is in the range of 20 to 600 ml, preferably 50 to 300 ml, particularly 100 to 200 ml per 1 m<sup>2</sup> of lightsensitive material. The shorter the development time is, the more remarkable is the effect of the present invention.

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When the reversal processing is effected, the color development is normally conducted after a blackand-white development. The black-and-white developing solution may comprise known black-and-white developing agents such as dihydroxybenzene, e.g., hydroquinone, 3-pyrazolidone, e.g., 1-phenyl-3pyrazolidone, and aminophenol, e.g., N-methyl-p-aminophenol, singly or in combination.

These color developing solution and black-and-white developing solution normally have a pH value of 9 to 12. The replenishing amount of these developing solutions depends on the type of the color photographic light-sensitive material to be processed but is normally in the range of 3 t per 1 m<sup>2</sup> of the light-sensitive

- 25 material. If the replenishing liquid of the developing solution has a reduced concentration of bromide ion, the replenishing amount thereof can be 500 ml or less. If the replenishing amount of the developing solution is reduced, the area of the processing tank in contact with air is preferably reduced to prevent the solution from being evaporated or oxidized by air. A means of restricting the accumulation of bromide ion in the developing solution may be used to reduce the supply amount of the developing solution.
- 30 The photographic emulsion layer which has been subjected to color development is normally then subjected to bleaching. The bleaching solution, blix solution and fixing solution to be used in the present invention will be further described hereinafter.

It is normally said that a bleaching solution or blix solution is unstable at a pH of 6 to 8. In the present invention, it has been found that the bleaching bath is more stable and more excellent in bleaching capability at a pH range of 3.5 to 5 than a pH value of 7. However, it was also found that a cyan die is converted to a leuco-compound in this pH range. The Inventors have found that this problem can be remarkably eliminated by drastically saving the amount of water to be supplied to the subsequent bath (e.g. rinse and stabilization). This approach also improves the bleaching capability. This approach further effectively eliminates stain which easily occurs after a processing with a two-equivalent coupler.

- As a bleaching agent for the present bleaching solution or blix solution there can be used any suitable bleaching agent. Particularly preferred examples of suitable bleaching agents include organic complex salts of iron (III) with organic acids such as aminopolycarboxylic acid, e.g., ethylenediaminetetraacetic acid, and diethylenetriaminepentaacetic acid, aminopolyphosphonic acid, phosphonocarboxylic acid, tartaric acid, and malic acid, persulfate, and hydroperoxide.
- 45 Particularly preferred among these compounds are organic complex salts of iron (III) in the light of rapidness of the development and pollution prevention. Examples of useful aminopolycarboxylic acid, aminopolyphosphonic acid, organic phosphonic acid, and salts thereof which can be used to form such organic complex salts of iron (III) include ethylenediaminetetraacetic acid, diethylenetraminepentaacetic acid, 1,3-diaminopropanetetraacetic acid, propylenediaminetetraacetic acid, nitrilotriacetic acid, cyclohex-
- anediaminetetraacetic acid, methyliminodiacetic acid, iminodiacetic acid, and glycoletherdiaminetetraacetic acid. These compounds may be sodium salts, potassium salts, lithium salts or ammonium salts. Particularly preferred among these compounds are complex salts or iron (III) with ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, 1,3-diaminopropanetetraacetic acid, and methyliminodiacetic acid.
- These ferric iron complex salts may be used in the form of a complex salt or may be formed of a ferric salt such as ferric sulfate, ferric chloride, ferric nitrate, ferric ammonium sulfate, and ferric phosphate, and a chelating agent such as aminopolycarboxylic acid, aminopolyphosphonic acid, and phosphonocarboxylic acid in a solution. Such a chelating agent may be used in excess of the stoichiometric amount for the

formation of the ferric ion complex salt. Particularly preferred among these iron complexes are aminopolycarboxylic acid-iron complexes. The amount of such an aminopolycarboxylic acid-iron complex to be added is in the range of 0.01 to 1.0 mol/t, preferably 0.05 to 0.50 mol/t.

The present bleaching solution, blix solution and/or pre-bath thereof may comprise various compounds as bleaching agents. Examples of suitable compounds excellent in bleaching capability include compounds containing a mercapto group or disulfide bound as described in U.S. Patent No. 3,893,858, West German Patent No. 1,290,812, Japanese Patent Application (OPI) No. 95,630/78, and Research Disclosure No. 17,129 (July 1978), thiourea compounds as described in Japanese Patent Publication No. 8,506/70, Japanese Patent Application (OPI) Nos. 20,832/77, and 32,735/78, and U.S. Patent No. 3,706,561, and compounds of halogen such as iodine, and bromine.

The present bleaching solution or blix solution may also contain a re-halogenating agent such as bromide, e.g., potassium bromide, sodium bromide, and ammonium bromide, chloride, e.g., potassium chloride, sodium chloride, and ammonium chloride, and iodide, e.g., ammonium iodide. The present bleaching solution or blix solution may optionally contain one or more corrosion inhibitors having a pH buffering capability such as inorganic acid, e.g., boric acid, borax, phosphinic acid, and phosphonic acid, organic acid, e.g., acetic acid, and tartaric acid, alkaline metal or ammonium salt thereof, e.g., sodium metaborate, sodium acetate, sodium carbonate, potassium carbonate, sodium phosphate, and sodium

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citrate, ammonium nitrate, and guanidine. The fixing agent to be used in the present blix solution or fixing solution may be a known fixing agent, i.e., a water-soluble silver halide solvent such as thiosulfate, e.g., sodium thiosulfate, and ammonium

thiosulfate, thiocyanate, e.g., sodium thiocyanate, and ammonium thiocyanate, thioether compound, e.g., ethylenebisthioglycolic acid, and 3,6-dithia-1,8-octanediol, and thiourea. These fixing agents may be used singly or in combination. Alternatively, a special blix solution made of a combination of a fixing agent as described in Japanese Patent Application (OPI) No. 155,354/80 and a large amount of a halide such as potassium iodide may be used in the present invention. In the present invention, a thiosulfate, particularly ammonium thiosulfate may be preferably used. The amount of such a fixing agent to be incorporated in the fixing or blix solution is preferably in the range of 0.3 to 2 mot, particularly 0.5 to 1.0 mot/t. The present fixing solution or blix solution may have a pH value of 3 to 10, preferably 5 to 9.

The present blix solution may contain a fluorescent brightening agent represented by the general formula (XI) in an amount of 0.1 to 10 g/t. The present blix solution may further contain various antifoam agents, surface active agents or organic solvents such as polyvinyl pyrrolidone, and methanol.

The present fixing solution or blix solution may contain as a preservative a sulfite ion-releasing compound such as sulfite, e.g., sodium sulfite, potassium sulfite, and ammonium sulfite, bisulfite, e.g., ammonium bisulfite, sodium bisulfite, and potassium bisulfite, and metabisulfite, e.g., potassium metabisulfite, sodium metabisulfite, and ammonium metabisulfite. Such a compound may be preferably used in an

amount of 0.02 to 0.50 mo *t*, *t*, particularly 0.04 to 0.40 mo *t*/*t* as calculated in terms of sulfite ion. As such a preservative there may be commonly used a sulfite. Other examples of suitable preservatives

As such a preservative there may be commonly used a sume. Other examples of catable preservative which may be used in the present invention include ascorbic acid, carbonyl-bisulfite addition product, and carbonyl compound.

The present fixing solution or blix solution may further contain a buffering agent, a chelating agent, an antifoam agent, and an antifungal agent as necessary.

In the present invention, the shorter the desilvering step is, the more remarkable is the effect of the present invention. In particular, the desilvering time is preferably 2 minutes or less, particularly 1 minute or less.

The rinsing solution or stabilizing bath may contain a fluorescent brightening agent represented by the general formula (XI) in an amount of 0.1 to 10 g/t.

The rinsing solution may further contain a surface active agent as a hydro-extracting agent or a chelating agent such as EDTA as a water softener.

The rinse step may be followed by the stabilizing step. Alternatively, the present light-sensitive material may be processed with aq stabilizing solution at first hand after being subjected to the fixing or blix step. Such a stabilizing solution may contain a compound which serves to stabilize images. Examples of such a compound include aldehyde compound such as formalin, buffering agent for adjusing the film pH to a value suitable for the stabilization of dyes, and ammonium compound. The stabilizing solution also may contain the above described various sterilizers or antifungal agents to inhibit proliferation of bacterial or render processed light-sensitive material fungi-resistant.

The stabilizing solution may further contain a surface active agent and a film hardener.

The amount of water to be used in the stabilizing step can drastically saved by employing the countercurrent process as in the rinse step by using 1 or less, preferably 0.5 or less. The supply of the

rinsing solution or stabilizing solution may be continuous or intermittent. In the latter case, the supply of the solution may be effected as necessary depending on the amount of the light-sensitive material to be processed or at predetermined time intervals.

The pH value of the solution to be used in the present rinse or stabilization step is in the range of 4 to 10, preferably 5 to 8. The temperature of the solution to be used in the present rinse or stabilization step can be widely selected depending on the application, characteristics, etc. of the light-sensitive material to be processed but is normally in the range of 15 to 45 °C, preferably 20 to 40 °C. The processing time can be freely selected. However, the shorter the processing time is, the more remarkable is the effect of the present invention. In the present invention, the processing time is preferably 30 seconds to 2 minutes, particularly 30 seconds to 1 minute and 30 seconds. The supply amount of the processing solution is

preferably small in the light or running cost, reduction in discharge and handleability. The less the supply amount of the processing solutions is, the more remarkable is the effect of the present invention.

The solution used in the rinse and/or stabilization step can be further used in the pre-baths. For example, the overflow of the rinsing water obtained by saving by the countercurrent process may be introduced into the pre-bath, e.g., blix bath which is supplied with a concentrated solution to reduce the amount of waste liquid.

The overflow liquid produced with the supply of the above described rinsing solution and/or stabilizing solution can be re-used in the other steps such as desilvering step.

The present silver halide color light-sensitive material may comprise a color developing agent for the purpose of simplifying and expediting the processing. To this end, such a color developing agent can be incorporated in the light-sensitive material in the form of various precursors thereof. Examples of such precursors of color developing agent include indoaniline compounds as described in U.S. Patent 3,342,597, Schiff base compounds as described in U.S. Patent 3,342,599, and Research Disclosure Nos. 14,850 and 15,159, aldol compounds as described in Research Disclosure No. 13,913, metal complexes as described

in U.S. Patent 3,719,492, and urethane compounds as described in Japanese Patent Application (OPI) No. 135,628/78,.

The present silver halide color light-sensitive material may optionally comprise various 1-phenyl-3-pyrazolidones for the purpose of accelerating color development. Typical examples of such compounds are described in Japanese Patent Application (OPI) Nos. 64,339/81, 144,547/82, and 115,438/83.

- The various processing solutions to be used in the present invention is used at a temperature of 10 to 50°C. The standard temperature range is normally between 33°C and 38°C. However, a higher temperature can be used to accelerate and shorten the processing. On the con-trary, a lower temperature can be used to improve the picture quality or the stability of the processing solu-tion. For the purpose of saving the amount of silver to be incorporated in the light-sensitive material, a processing using cobalt intensification or hydrogen peroxide intensification as described in West German Patent No. 2,226,770, and U.S. Patent
- 3,674,499 may be effected.

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- In the present invention, the sum of the time required for the blix step and the rinse or stabilization step is preferably 3 minutes or less.
- The process of the present invention can be applied to any processing with a color developing solution. For example, the process of the present invention can be applied to the processing of color paper, color reversal paper, color direct positive light-sensitive material, color positive film, color negative film, color reversal film, or the like. Particularly, the process of the present invention is useful in the processing of color paper or color reversal paper which is susceptible to stain.
- As the silver halide emulsion to be incorporated in the direct positive color printing light-sensitive material or color reversal printing light-sensitive material which is suitable for band stop filter of the present invention there may be preferably used a silver halide emulsion having the above described halogen composition comprising internal latent image type particulate silver halide having a multistructure as described in Japanese Patent Application No. 25,737/87.

As the silver halide emulsion to be incorporated in the color reversal printing light-sensitive material there may be preferably used an emulsion as described in European Patent No. 0217353A-2, and Japanese Patent Application (OPI) Nos. 39,043/86, and 61,156/86.

For an outer color reversal film, a soluble coupler is used instead of a hydrophobic coupler. Such a soluble coupler is incorporated in the color developing solution rather than the light-sensitive material.

The details of an internal latent image type emulsion and particulate silver halide which can be used in the present direct positive light-sensitive system such as autopositive color film and autopositive color paper are described in Japanese Patent Application (OPI) No. 81,337/88, left bottom on page 4 to right bottom on page 5.

Such an internal latent image type emulsion may be of the conversion type of the core/shell type,

preferably of the core shell type.

The details of the color couplers which can be used in the direct positive system are described in Japanese Patent Application (OPI) No. 81,337 88, left top on page 6 to left top on page 8. The details of various compounds which can be incorporated in the present light-sensitive material (e.g., color fog inhibitor, discoloration inhibitor, and dye) are described in Japanese Patent Application (OPI) No. 81,337/88, right top to right bottom on page 8.

In the present invention, if a direct positive color light-sensitive material is used, the direct positive color light-sensitive material which has been subjected to imagewise exposure is preferably then subjected to color development with a surface developing solution containing an aromatic primary amine color develop-

<sup>10</sup> ing agent and preferably having a pH value of 12 or less subsequently after or simultaneously with a fogging process with light or a nucleating agent, and then to blix to provide a direct positive color image. More preferably, the developing solution has a pH value of 10.0 to 11.0.

The fogging process to be used in the present invention can be accomplished by a so-called "light fogging process" in which the second exposure is provided over the entire surface of the light-sensitive

15 layer or a so-called "chemical fogging process" in which the development is effected in the presence of a nucleating agent. The development may be effected in the presence of a nucleating agent and a fogging light. Alternatively, a light-sensitive material containing a nucleating agent may be subjected to fog exposure.

The details of the light fogging process are described in the above cited Japanese Patent Application (OPI) No. 81,337 88, left bottom on page 9 to left bottom on page 10. The details of nucleating agents which can be used in the present invention are described in the above described Japanese Patent Application (OPI) No. 81,337/88, right top on page 10 to left top on page 14. Particularly, the compounds represented by the general formulas [N-1] and [N-2] described in the same patent may be preferably used.

The details of nucleating accelerators which can be used in the present invention are described in the same Japanese Patent Application (OPI), left top to right bottom on page 15. Specific examples of such nucleating accelerators which can be preferably used in the present invention include compounds (A-1) to (A-13) shown in the same Japanese Patent Application (OPI), page 15.

Furthermore, examples of color diffusion transfer light-sensitive materials and color image formation processes which can be used in the present invention are described in U.S. Patent No. 3,415,644 for those

<sup>30</sup> using a dye developing agent, in T. H. James, "The Theory of Photographic Process", 4th ed., 1977, Chapter 12 for those using a diffusive dye-releasing coupler, and in "Photographic Science and Engineering", Vol. 20, No. 4, pp. 155-164, July and August 1976 for those using a diffusive dye-releasing redox compound.

On the other hand, the details of heat-developable color light-sensitive material and color formation process which can use the present invention are described in Japanese Patent Application (OPI) No. 58,543/83.

The present invention will be further described in the following examples, but the present invention should not be construed as being limited thereto.

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### EXAMPLE 1

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# Preparation of color light-sensitive material for use in photographing

A multilayer color light-sensitive material specimen 101 was prepared by coating various layers of the undermentioned compositions on an undercoated cellulose triacetate film support.

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#### Composition of light-sensitive layer

The value of the coated amount of each component is represented in g/m<sup>2</sup>. The coated amount of silver halide is represented in terms of amount of silver. The coated amount of sensitizing dye is represented by molar amount thereof per 1 mot of silver halide contained in the same layer. 1st layer: antihalation layer

Black co	0.2	
Gelatin	1.4	
UV-1	0.02	
UV-2	0.04	
UV-3	0.04	
Solv-1	0.05	

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#### 2nd layer: intermediate layer

Finely divided particles of silver bromide (average particle diameter: 0.07 µm) 0.08

15	Gelatin	1.1
	ExC-1	0.02
	ExM-1	0.06
	UV-1	0.03
	UV-2	0.06
20	UV-3	0.07
	Cpd-1	0.1
	ExF-1	0.004
	Solv-1	0.1
	Solv-2	0.09

25

### 3rd layer: low sensitivity réd-sensitive emulsion layer

30 Silver bromoiodide emulsion (Agl content: 6.3 mol %; internal high Agl type; c/s ratio: 1/1; diameter in terms of sphere: 0.8 μm; coefficient of fluctuation in diameter in terms of sphere: 25 %; tabular particles; diameter thickness ratio: 2) 1.5

	Gelatin	1.7
	ExC-2	0.3
35	ExC-3	0.02
	ExS-1	7.1 x 10 <sup>−5</sup>
	ExS-2	1.9 x 10 <sup>−5</sup>
	ExS-3	2.4 x 10 <sup>−₄</sup>
	ExS-4	4.2 x 10 <sup>−5</sup>
40	Solv-2	0.03

# 4th layer: middle sensitivity red-sensitive emulsion layer

45

Silver bromoiodide emulsion (Agl content: 4.8 mo  $\ell$  %; internal high Agl type; c/s ratio: 1/4; diameter in terms of sphere: 0.9  $\mu$ m; coefficient of fluctuation in diameter in terms of sphere: 50%; tabular particles; diameter/thickness ratio: 1.5) 1.4

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Gelatin 2.1 ExC-2 50 0.4 ExC-3 0.002 ExS-1 5.2 x 10<sup>-5</sup> ExS-2 1.4 x 10<sup>-5</sup> ExS-3 1.8 x 10<sup>-4</sup> ExS-4 3.1 x 10<sup>-5</sup> 55 Solv-2 0.5

## 5th layer: high sensitivity red-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 10.2 mot %; internal high Agl type; c/s ratio: 1/2; diameter in terms of sphere: 1.2 µm; coefficient of fluctuation in diameter in terms of sphere: 35 %; tabular particles; diameter thickness ratio: 3.5) 2.1

	Gelatin	2.0
	ExC-1	0.06
	ExC-4	0.04
	ExC-5	0.2
10	ExS-1	6.5 x 10 <sup>-5</sup>
	ExS-2	1.7 x 10 <sup>−5</sup>
	ExS-3	2.2 x 10 <sup>−</sup>
	ExS-4	3.8 x 10 <sup>−5</sup>
	Solv-1	0.1
15	Solv-2	0.3

6th layer: intermediate layer

0.8

20

5

Gelatin 1.1

# 25 7th layer: low sensitivity green-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 6.3 mot %; internal high Agl type; c/s ratio: 1/1; diameter in terms of sphere: 0.8  $\mu$ m; coefficient of fluctuation in diameter in terms of sphere: 25 %; tabular particles; diameter/thickness ratio: 2) 0.6

	ExM-2	0.3
	ExM-1	0.03
	ExY-1	0.04
	ExS-5	3.1 x 10 <sup>−5</sup>
35	ExS-6	$1.0 \times 10^{-4}$
	ExS-7	3.8 x 10 <sup>−4</sup>
	H-1	0.04
	H-2	0.01
	Solv-2	0.2

40

# 8th layer: middle sensitivity green-sensitive emulsion layer

45 Silver bromoiodide emulsion (Agl content: 4.8 mot %; internal high Agl type; c/s ratio: 1/4; diameter in terms of sphere: 0.9 μm; coefficient of fluctuation in diameter in terms of sphere: 50 %; tabular particles; diameter/thickness ratio: 1.5) 1.1

	Gelatin	1.4
	ExM-4	0.2
50	ExM-5	0.05
	ExM-1	0.01
	ExM-3	0.01
	ExY-1	0.02
	ExS-5	2.0 x 10 <sup>-5</sup>
55	ExS-6	7.0 x 10 <sup>-5</sup>
	ExS-7	2.6 x 10 <sup>−4</sup>
	H-1	0.07

H-2 0.02 Solv-1 0.06 Solv-2 0.4

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9th layer: high sensitivity green-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 10.2 mot %; internal high Agl type; c/s ratio: 1/2; diameter in terms of sphere: 1.2 µm; coefficient of fluctuation in diameter in terms of sphere: 38 %; tabular particles; diameter thickness ratio: 4) 2.1

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	Gelatin	2.2
	ExC-2	0.02
	ExM-5	0.1
15	ExM-1	0.05
	ExS-5	3.5 x 10 <sup>−5</sup>
	ExS-6	8.0 x 10 <sup>-5</sup>
	ExS-7	3.0 x 10 <sup>−4</sup>
	Solv-1	0.08
20	Solv-2	0.7

10th layer: yellow filter layer

Yellow colloidal silver 0.08 Gelatin 1.0 Cpd-1 0.1

30

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# 11th layer: low sensitivity blue-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 9.0 mot %; internal high Agl type; c/s ratio: 1/2; diameter in terms of sphere: 0.75 μm; coefficient of fluctuation in diameter in terms of sphere: 21 %; octahedron particles; diameter/thickness ratio: 1) 0.3

 Gelatin
 1.3

 ExY-2
 0.7

 ExY-1
 0.03

 H-1
 0.03

 H-2
 0.01

 Solv-2
 0.3

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# 12th layer: middle sensitivity blue-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 10.2 mot %; internal high Agl type; c/s ratio: 1/2; diameter in terms of sphere; 1.0 μm; coefficient of fluctuation in diameter in terms of sphere: 30 %; tabular particles; diameter/thickness ratio: 3.5) 0.4

Gelatin0.7ExY-20.1ExS-8 $2.2 \times 10^{-4}$ H-10.01H-20.005Solv-20.05

# 13th layer: high sensitivity blue-sensitive emulsion layer

Silver bromoiodide emulsion (Agl content: 9.8 mot %; internal high Agl type; c/s ratio: 1/2; diameter in terms of sphere: 1.8 μm; coefficient of fluctuation in diameter in terms of sphere: 55 %; tabular particles; diameter thickenss ratio: 4.5) 0.8

 Gelatin
 0.7

 ExY-2
 0.2

 ExS-8
 2.3 x 10<sup>-4</sup>

 Solv-2
 0.07

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14th layer: 1st protective layer

15	Gelatin	0.9
	UV-4	0.1
	UV <b>-</b> 5	0.2
	H-1	0.02
	H-2	0.005
20	Solv-3	0.03
	Cpd-2	0.7

25 15th layer: 2nd protective layer

Emulsion of finely divided particles of silver bromide (average particle diameter: 0.07 μm)0.1Gelatin0.7H-10.2H-20.05

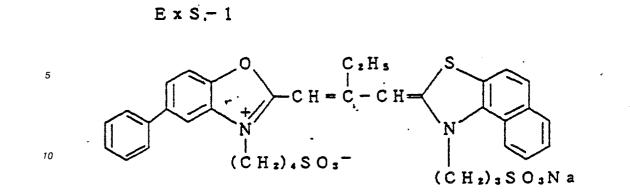
35

30

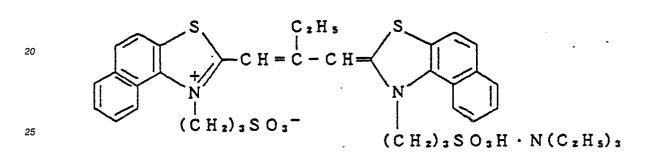
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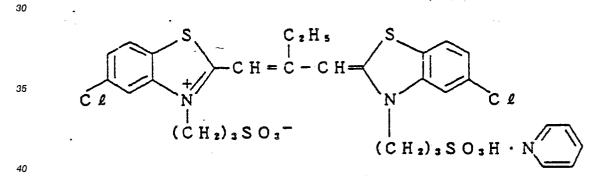
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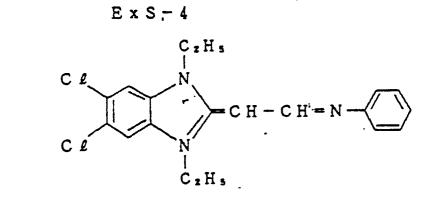


E x S - 2

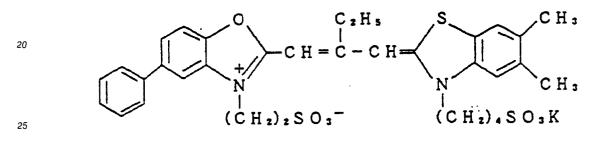


 $E \times S - 3$ 

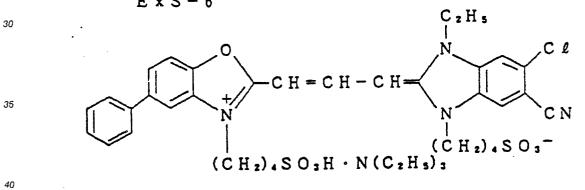


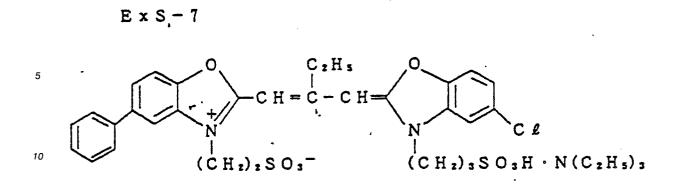


 $E \times S - 5$ 

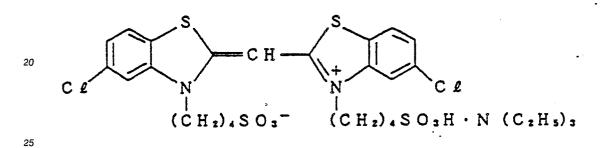


 $E \times S - 6$ 

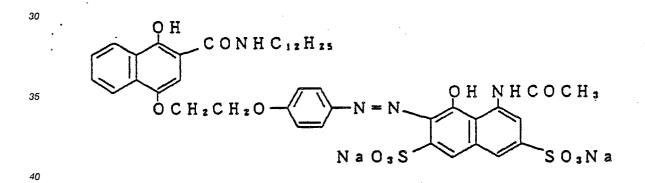




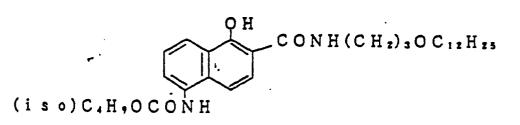
E x S - 8



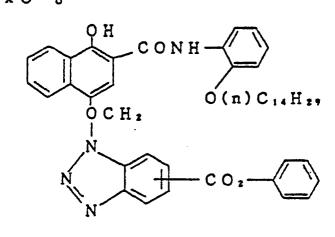
 $E \times C = 1$ 



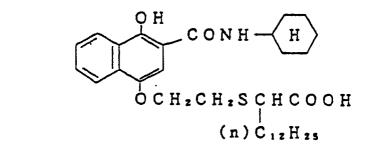


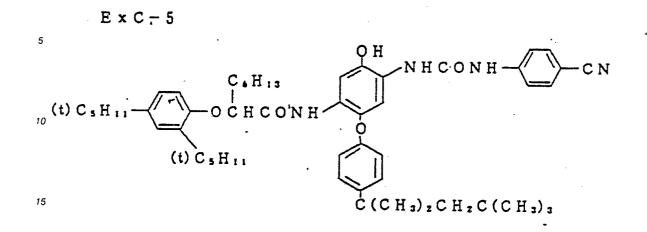


E x C - 3



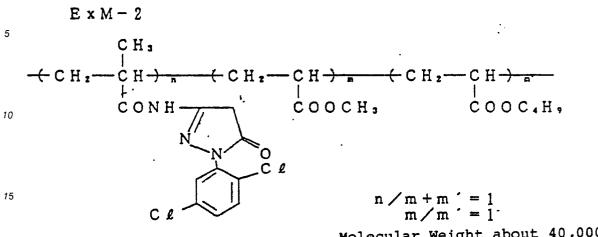
E x C - 4

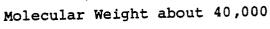




$$E \times M = 1$$

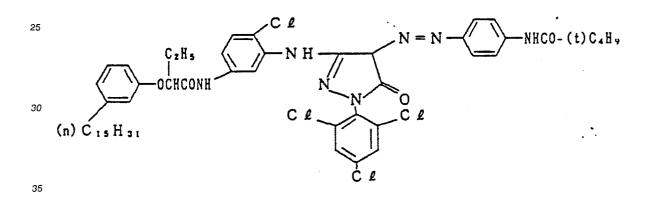
 $C_{2}H_{3}$   $C_{2}H_{3}$   $C_{2}H_{3}$   $C_{2}H_{3}$   $C_{2}H_{3}$   $C_{2}H_{3}$   $C_{3}H_{11}$   $C_{3}H_{11}$ 



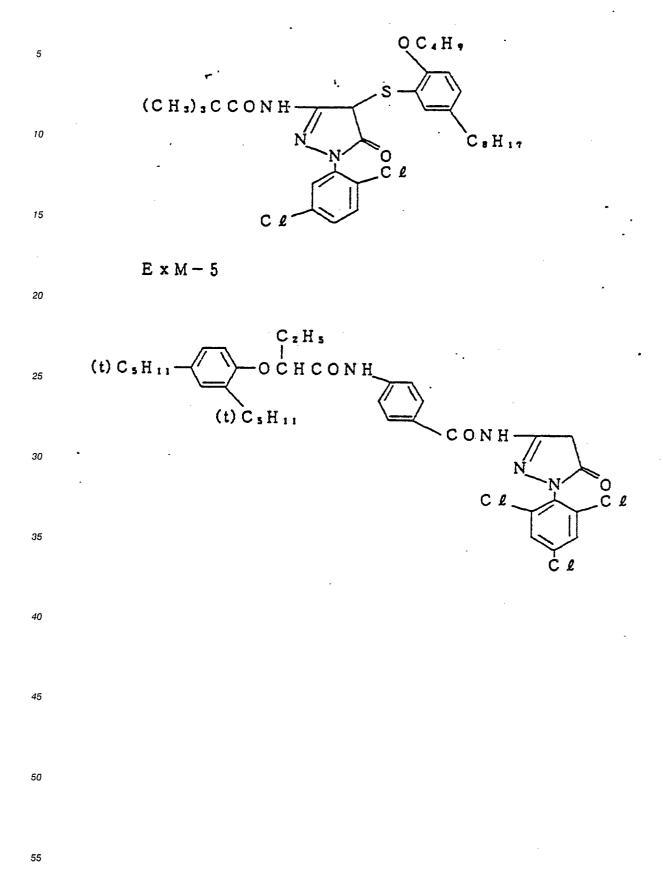


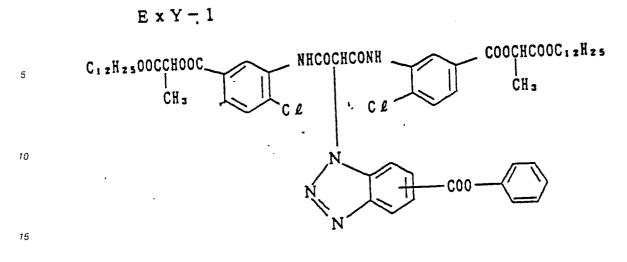
.

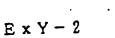
 $E \times M - 3$ 



 $E \times M - 4$ 







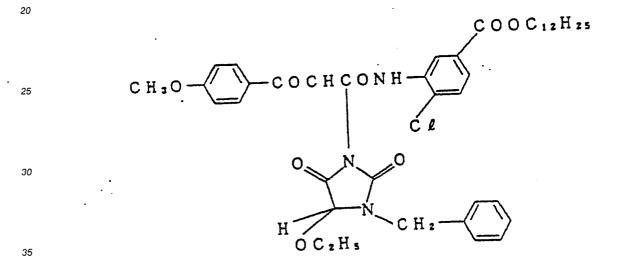
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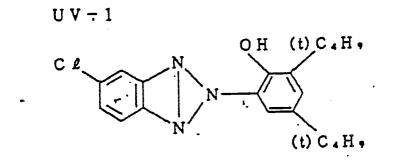
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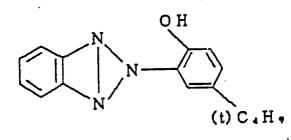
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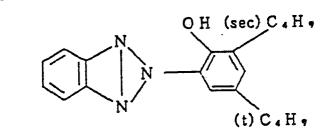


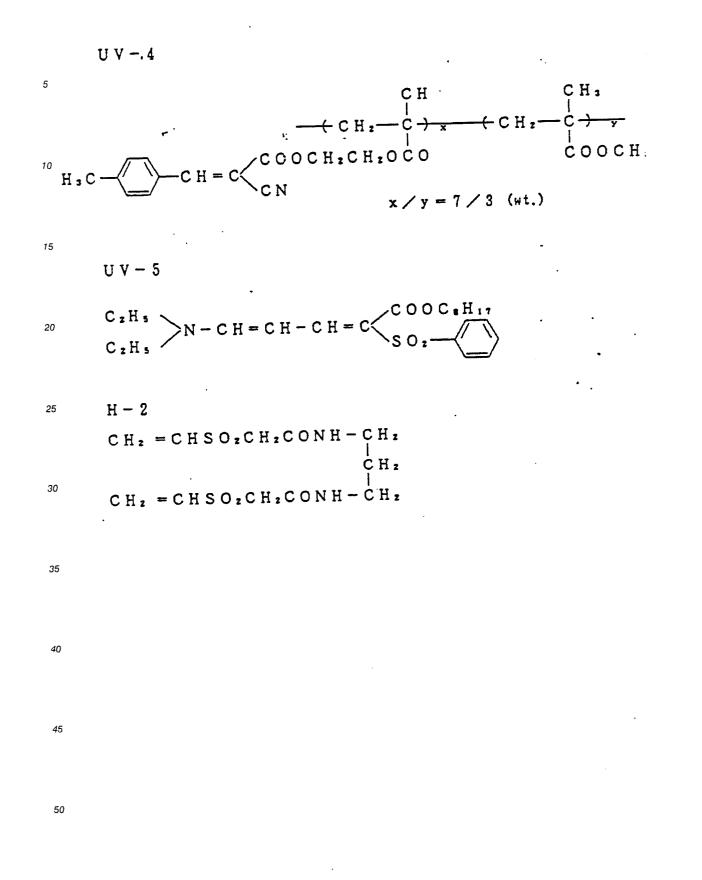


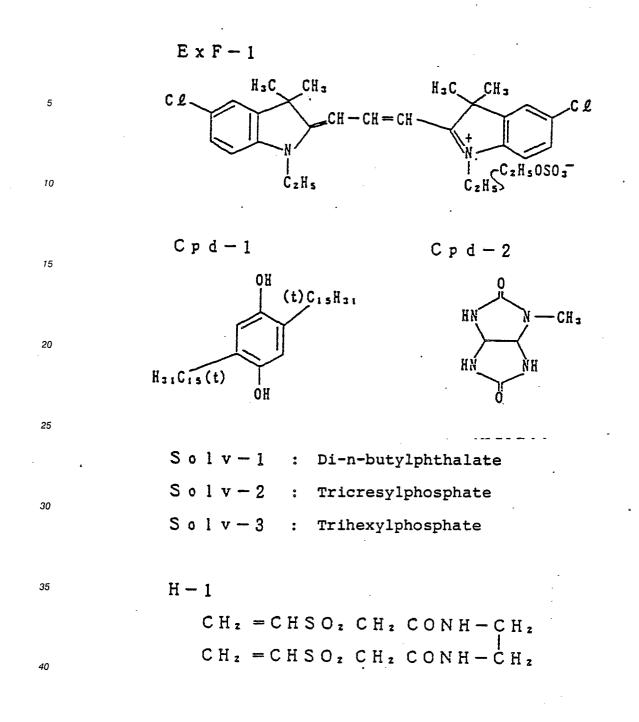
U V - 2



UV-3







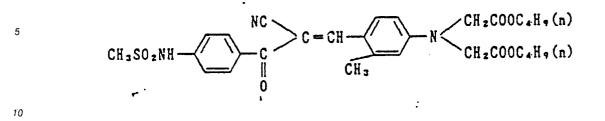
## Preparation of Specimen 102

Specimen 102 was prepared in the same manner as in Specimen 101 except in that 0.2 g of Compound C of the undermentioned general formula was added to the 10th layer in stead of the yellow colloidal silver, ExM-4 and ExM-5 were replaced by the above described ecemplary compound (VIII)-2 and ExY-2 was replaced by the above described exemplary compound (X)-(7).

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- Compound C



(Yellow dye described in Japanese Patent Application (OPI) No. 205,934/86)

Color development of color light-sensitive material for use in photographing

20 Processing							
Step	Processing time Processing t	cemperature					
Color development	3 min. 15 sec. 38 °C						
<sup>25</sup> Bleaching	1 min. 00 sec. "						
Blix	3 min. 15 sec. "						
Rinse (1)	40 sec. 35 °C						
<sup>30</sup> Rinse (2)	1 min. 00 sec. "						
35 Stabilization	40 sec.	38 °C					
Drying	l min. 15 sec.	55 °C					

40

15

The composition of various processing solutions used in the above processing steps were as follows:

45

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# Color developing solution

		(unit: g)
5	Diethylenetriaminepentaacetic acid	1.0
	l-Hydroxyethylidene-1,l-diphosphonic aci	d 3.0
10	Sodium sulfate .	4.0
10	Potassium carbonate	30.0
	Potassium bromide	30.0 1.4 1.5 mg
15	Potassium iodide	1.5 mg
	Hydroxylamine sulfate	2.4
20	Water to make	1.0 1
	PH	10.05

25

# Bleaching solution

(unit: g)

30	Ferric ammonium ethylenediaminetetraace	etate .
	(dihydrate)	120.0
	Disodium ethylenediamine tetraacetate	10.0
35	Ammonium bromide	100.0
	Ammonium nitrate	10.0
40	Bleach accelerator	0.005 mol

45  $\begin{pmatrix} H_{3}C \\ H_{3}C \end{pmatrix} N - C H_{2} - C H_{2} - S \end{pmatrix} \cdot 2 H C \ell$ 50 Aqueous ammonia (27 %) 15.0 ml
Water to make 1.0  $\ell$ pH 6.3

# Blix solution

# (unit: g)

5 F	erric ammonium ethylenediamine tetraacetate	8	
(	dihydrate)	50.0	
	isodium ethylenediamine tetraacetate	5.0	
10 S	Sodium sulfite	12.0	
A	queous solution of ammonium thiosulfate		
15 (	(70 %)	240.0	m <b>£</b>
F	Aqueous ammonia (27 %)	6.0	m L
<b>6</b>	Vater to make	1.0	L
	pH	7.2	

#### **Rinsing solution**

Tap water was passed through a mixed bed type column filled with a strongly acidic H type exchange 30 resin (Rome & Herse Corp's Amberlite IR-120B) and an OH type anionic exchange resin (Amberlite IR-400) so that the calcium and magnesium concentration was adjusted to 3 mg/t or less. Sodium dichlorinated isocyanurate and sodium sulfate were added to the water thus treated in amounts of 20 mg/t and 150 mg/t, respectively.

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The pH value of the rinsing solution thus prepared was in the range of 6.5 to 7.5.

Stabilizing solution

		(unit: g)
40	Formalin (37 %)	2.0 ml
	Polyoxyethylene-p-monononylphenylether (aver	age
45	polymerization degree: 10)	0.3
	Disodium ethylenediaminetetraacetate	0.05
	Water to make	1.0 1
50	pH	5.0 - 8.0

The color light-sensitive material specimen 101 thus prepared was then exposed to light from a standard light source for use in photographing (about 5,500 °K) through a Macbeth chart. The specimen 55 thus exposed was then subjected to the above described color development to obtain a color negative film. The spectral transmittance curve T ( $\lambda$ ) for the various coloring materials contained in the color negative film were then obtained. Furthermore, the specimen 101 was exposed to light through a Macbeth chart No. 22

(achromatic chart; optical density: about 0.7). The image on the film was then printed on a color printing paper (Fuji Photo Film Co., Ltd.'s Super HR) by means of a printer. The printing paper was then subjected to processing with Fuji Photo Film Co., Ltd.'s standard developing solution CP-20 to obtain a grey color print. On the other hand, the spectral sensitivity distribution S ( $\lambda$ ) (modified so as to give the same energy) of the color printing paper was obtained. The energy distribution of a light source for printing  $p(\lambda)$  was

5 of the color determined.

The effective spectral sensitive energy distribution E ( $\lambda$ ) for the each light-sensitive layers were obtained by the following equations:

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 $\begin{array}{ll} \mathsf{E}_{b}(\lambda) = S_{b}(\lambda) \bullet \mathsf{T}_{y}(\lambda) \bullet \mathsf{P}(\lambda) & (3) \\ \mathsf{E}_{g}(\lambda) = S_{g}(\lambda) \bullet \mathsf{T}_{m}(\lambda) \bullet \mathsf{P}(\lambda) & (4) \\ \mathsf{E}_{r}(\lambda) = S_{r}(\lambda) \bullet \mathsf{T}_{c}(\lambda) \bullet \mathsf{P}(\lambda) & (5) \end{array}$ 

The results are shown in Figure 1-(a). The characteristics concerning the mutual independence of the various light-sensitive layers are shown in Table 1. The results show that only  $E_r(\lambda)$  is independent.

15

Ta	ble	1

20 Specimen	used	····		Sp	ecimer	n 101 and	Super	HR	Paper
E(人) )	E <sub>b</sub> (入)			Fig.	l-(a)	E <sub>b</sub> (入)			
25 <sub>.</sub> ]	e <sub>g</sub> (				11	E <sub>g</sub> ( 人)			
]	E <sub>r</sub> (入)				fi	E <sub>r</sub> (入)			
E <sup>max</sup> g(入)/E <sup>r</sup> b	max) át	400-485	mm .		••	0.20			
<sup>30</sup> Er(X)/Eb max max	(人) at	400-485	mm			0.03 >			
E <sub>b</sub> (λ)/E <sub>g</sub>						0.20			
<sup>E<sup>max</sup><sub>35</sub>r(λ)/E<sup>ax</sup><sub>g</sub></sup>	(人) at	485-570	mm			0.01 >			
E <sup>max</sup> b(人)/Er	(人)at	570-750	mm			0.01 >			
E <sup>max</sup> g(λ)/E <sup>max</sup> r	(ر) at	570-750	mm			0.01 >			
<sup>40</sup> E <sub>g</sub> /E <sub>b</sub> at	400-485	mm				0.2			
E <sub>r</sub> /E <sub>b</sub> at	400-485	mm				0.01 >			
45									
E <sub>b</sub> /E <sub>g</sub> at	485-570	mm				0.11			
<sup>50</sup> E <sub>r</sub> /E <sub>b</sub> at	485-570	mm				0.01 >			
E <sub>b</sub> /E <sub>r</sub> at						0.01 >			•
Eg/Er at	570-750	) mm		• • • • • • • • • • • • • • • • • • • •		0.01 >			

55

The image on the negative film was then printed on a color printing paper (Fuji Photo Film Co., Ltd.'s Super HR) with a multi-layer dielectric compound deposited film, having a spectral transparent curve as is

shown in Fig. 3-(a), interposed between a light source and the negative film. The color printing paper thus printed was then subjected to the above described processing with CP-20 to obtain a grey color print.

The results of  $E_b(\lambda)$ ,  $E_g(\lambda)$ , and  $E_r(\lambda)$  are shown in Figure 2-(a). The results show that  $E_r(\lambda)$  and  $E_g(\lambda)$  are independent.

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#### EXAMPLE 2

10

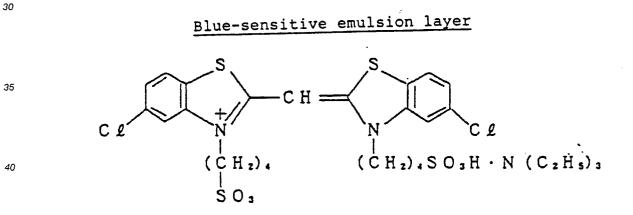
#### Preparation of multilayer color printing light-sensitive Material

A multilayer color printing paper specimen 201 was prepared by coating various layers of the undermentioned compositions on a paper support laminated with polyethylene on the both sides thereof.

#### Preparation of coating solution for 1st layer

19.1 g of a yellow coupler (ExY) and 4.4 g of a dye stabilizer (Cpd-1) were dissolved in 27.2 cc of ethyl acetate and 7.7 cc of a solvent (Solv-1). The solution thus obtained was then emulsion-dispersed in 185 cc of a 10% aqueous solution of gelatin containing 8 cc of 10 % sodium dodecylbenzenesulfonate. On the other hand, a blue-sensitive sensitizing dye was added to a silver bromochloride emulsion (containing 80.0 mot % of silver bromide and 70 g/kg of Ag) in an amount of 5.0 x 10<sup>-4</sup> mot per 1 mot of silver to prepare an emulsion. The emulsion dispersion and the emulsion thus obtained were mixed to prepare a 1st layer coating solution having the undermentioned composition. Coating solutions for the 2nd layer to the 7th layer were then prepared in the same manner as described above. As a gelatin hardener for the various layers there was used sodium 1-oxy-3,5-dichloro-s-triazine.

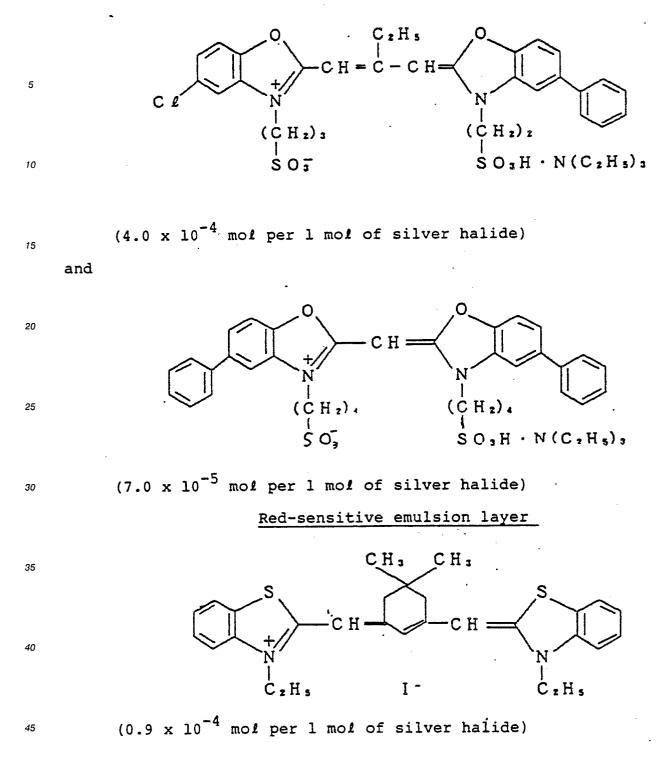
As spectral sensitizing dyes for the various layers there were used the following compounds:



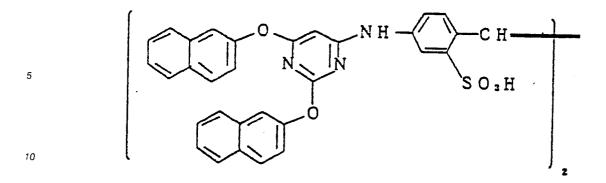
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(5.0 x 10<sup>-4</sup> mol per 1 mol of silver halide) Green-sensitive emulsion layer

50



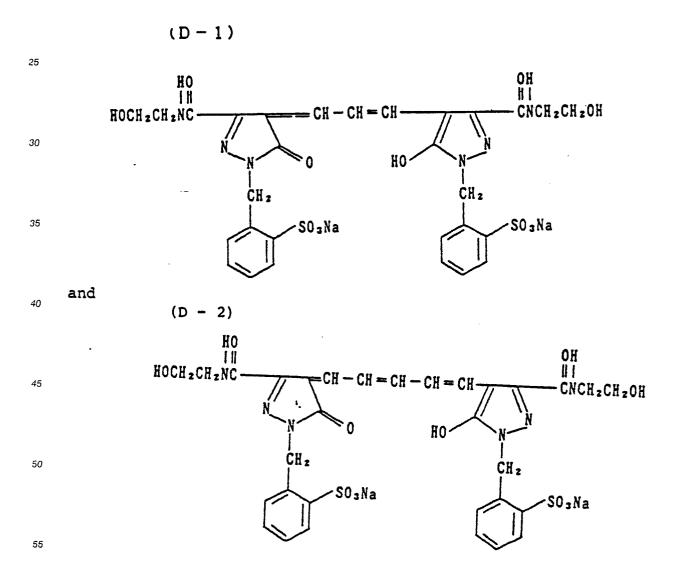
A compound of the undermentioned general formula was incorporated in the red-sensitive emulsion layer in an amount of  $2.6 \times 10^{-3}$  moll per 1 moll of silver halide.



1-(5-Methylureidephenyl)-5-mercaptotetrazole was incorporated in the blue-sensitive emulsion layer, the $green-sensitive emulsion layer and the red-sensitive emulsion layer in amounts of 4.0 x <math>10^{-6}$  mot, 3.3 x  $10^{-5}$  mot and 1.0 x  $10^{-5}$  mot per 1 mot of silver halide, respectively.

4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene was incorporated in the blue-sensitive emulsion layer and the green-sensitive emulsion layer in amounts of  $1.2 \times 10^{-2}$  mol and  $1.1 \times 10^{-2}$  mol per 1 mol of silver halide, respectively.

20 For the purpose of inhibiting irradiation, the undermentioned dyes were incorporated in the emulsion layer.



#### Layer construction

The composition of the various layers will be described hereinafter. The value of the coated amount of seach component is represented in g/m<sup>2</sup>. The coated amount of silver halide emulsion is represented in terms of amount of silver.

Polyethylene laminated paper (Polyethylene at the first layer side contains white pigment (TiO<sub>2</sub>) and blue dye (ultramarine)).

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## Support

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# 1st layer (Blue-sensitive layer)

Silver halide emulsion (Br: 80%)0.26Gelatin1.83Yellow coupler (ExY)0.83

Dye stabilizer (Cpd-1) 0.19 Solvent (Solv-1) 0.35

25

# 2nd layer (Color mixing inhibiting layer)

Gelatin 0.99 Color mixing inhibitor (Cpd-2) 0.08

30

# 3rd layer (Green-sensitive layer)

Silver halide emulsion (Br: 80 %) 0.16 35 Gelatin 1.79 Magenta coupler (ExM) 0.32 0.20 Dye stabilizer (Cpd-3) Dye stabilizer (Cpd-4) 0.01 Solvent (Solv-2) 0.65 40 Dye stabilizer (Cpd-8) 0.06 Dye stabilizer (Cpd-9) 0.06 Dye (D-1) 0.10

45

# 4th layer (ultraviolet absorbing layer)

Gelatin 1.58 50 Ultraviolet absorber (UV-1) 0.62 Color mixing inhibitor (Cpd-5) 0.05 Solvent (Solv-3) 0.24

# 5th layer (red-sensitive layer)

Silver halide emulsion (Br: 70 %) 0.23 Gelatin 1.34 Cyan coupler (ExC) 0.34 Dye stabilizer (Cpd-6) 0.17 Polymer (Cpd-7) 0.40 Solvent (Solv-4) 0.23 Dye (D-2) 0.12

10

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# 6th layer (ultraviolet absorbing layer)

15<sup>°</sup> Gelatin 0.53 Ultraviolet absorber (UV-1) 0.21 Solvent (Solv-3) 0.08

20

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# 7th layer (protective layer)

Gelatin1.33Acryl-modified copolymer of polyvinyl alcohol (modification degree: 17%)0.17Liquid paraffin0.03

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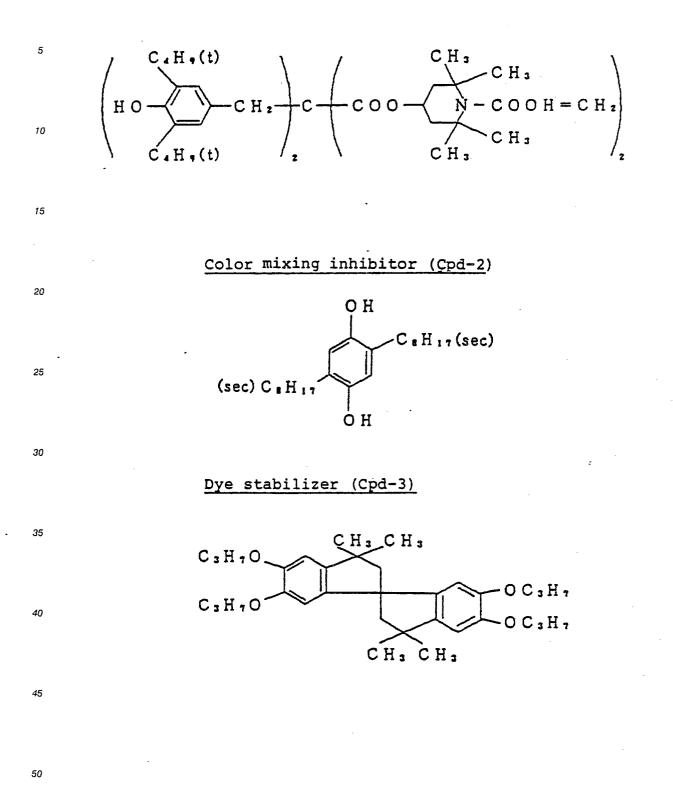
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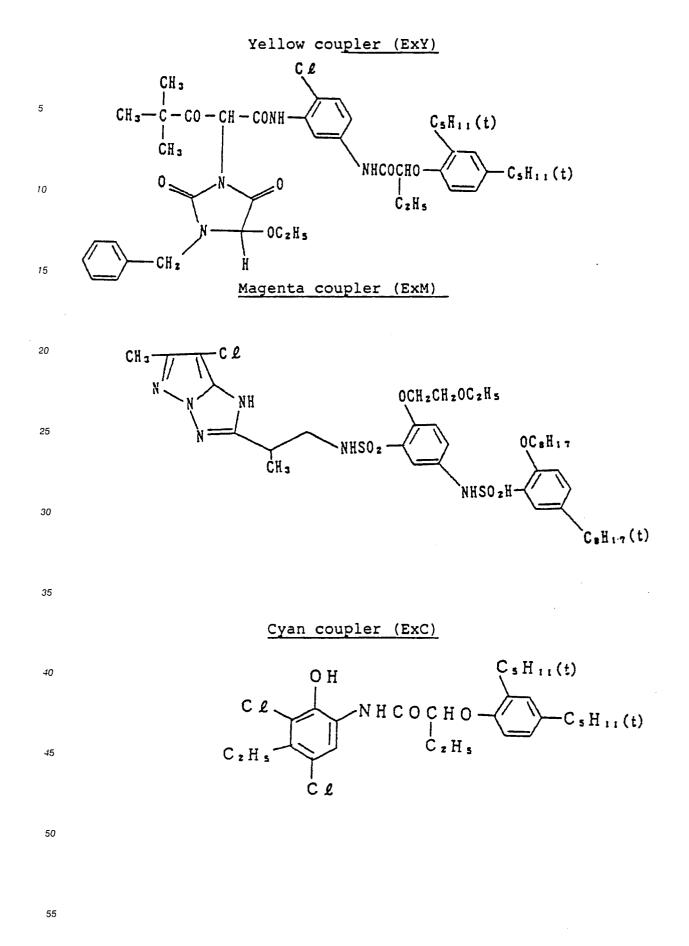
# 40

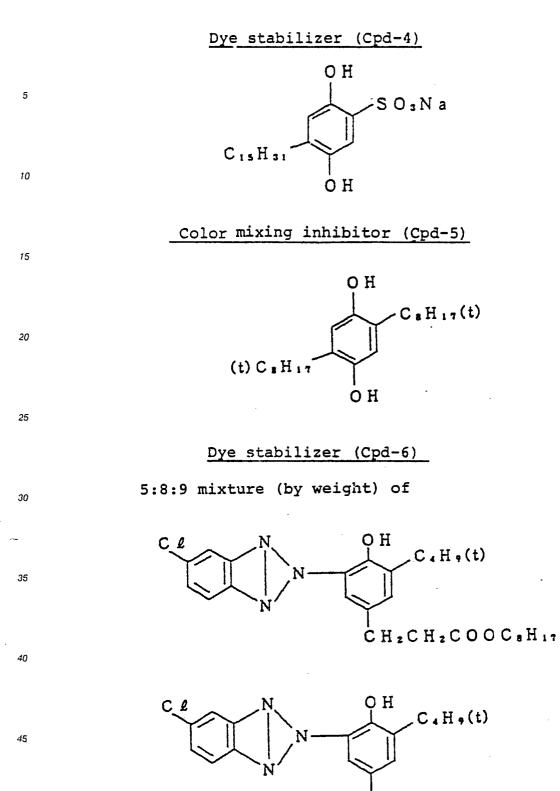
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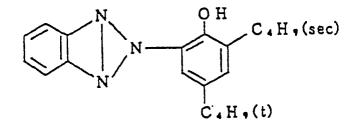
50

# Dye stabilizer (Cpd-1)









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Polymer (Cpd-7)

 $--(CH_2 - CH_{-}) - \frac{1}{R}$ 

Average molecular weight 80,000

Ultraviolet absorber (UV-1)

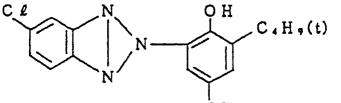
25

30

35

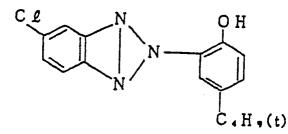
40

2 : 9 : 8 mixture (by weight) of



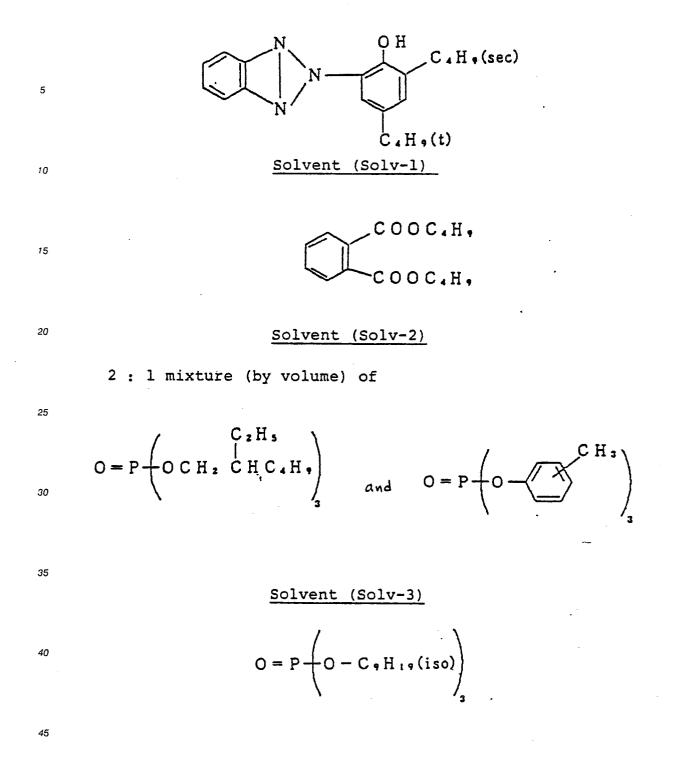
ĊH<sub>2</sub>CH<sub>2</sub>COOC<sub>8</sub>H<sub>17</sub>

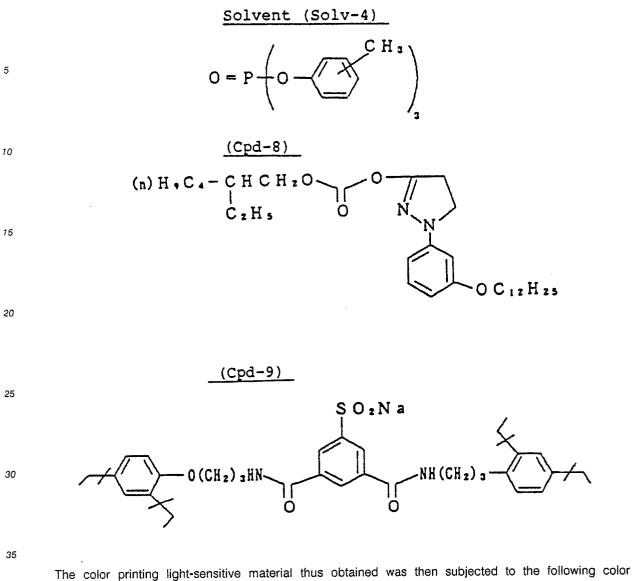
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The color printing light-sensitive material thus obtained was then subjected to the following color development.

40	Processing step	Temperat	ure	Time
	Color development	35 °C		45 sec.
	Blix	30-36	°C	45 sec.
45	Stabilization 1	30-37	°C	20 sec.
	Stabilization 2	30-37	°C	20 sec.
50	Stabilization 3	30-37	°C	20 sec.
	Stabilization 4	30-37	°C	30 sec.
	Drying	70-85	°C	60 sec.

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(The stabilizing step was effected in a countercurrent process in which water flows from the tank 4 to the tank 1 through the tank 3 and the tank 2).

The composition of the various processing solutions were as follows:

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# Color developing solution

Water 800 m t Ethylenediaminetetraacetic acid 2.0 q Triethanol amine 8.0 g 10 Ammonium sodium chloride 1.4 g Disodium ethylenediaminetetraacetate 3 g Potassium carbonate 25 g N-ethyl-N-(ß-methanesulfoamidoethyl)-3-methyl-4-aminoaniline sulfate 5.0 g N,N-diethylhydroxylamine 4.2 g 15 5,6-Dihydroxybenzene-1,2,4-trisulfonic acid 0.3 g Fluorescent brightening agent (4,4 -diaminostylbene series) 2.0 g Water to make 1,000 mt pH at 25 °C 10.10 20

## Blix solution

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Water 400 m t Ammonium thiosulfate (70 %) 100 m t Sodium sulfite 18 g 30 Ferric ethylenediaminetetraacetate 55 g Glacial acetic acid 8 g Water to make 1,000 m t pH at 25 °C 6.5

#### 35

## Stabilizing solution

- Formalin (37 %) 0.1 g
  Formalin-sulfite addition product 0.7 g
  5-Chloro-2-methyl-isothiazoline-3-one 0.02 g
  2-Methyl-4-isothiazoline-3-one 0.01 g
  Copper sulfate 0.005 g
  Water to make 1.000 m t
- 45 Water to make 1,000 m t pH at 25 °C 4.0

Specimen 202 was prepared in the same manner as in Specimen 201 except in that the silver halide emulsion (Br: 80 mot %) to be incorporated in the 1st layer was replaced by the silver halide emulsion A (Br: 0.5 mot %) shown below and the silver halide emulsion B (Br: 1.0 mpt %) shown below was incorporated in the 3rd layer.

#### Preparation of Emulsion (A)

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Formation of host particulate silver chloride

# Solution 1

.  $H_2O$ 1,000 cc NaCt 5.5 g 5 Gelatin 32 g Solution 2 10 Sulfuric acid (1 N) 24 cc 15 -Solution 3 Compound A of the general formula (1%); 20 Compound A CH<sub>3</sub> 25 N٠ S I ĊH3 30 Solution 4 35 NaCt 1.7 g H<sub>2</sub>O 200 g 40

Solution 5

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3 cc

<sup>45</sup> AgNO<sub>3</sub> 5 g H<sub>2</sub>O to make 200 cc

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Solution 6

 $\begin{array}{rl} & \text{NaCl} & 41.3 \text{ g} \\ & \text{K}_2 \text{IrCl}_6 \ (0.001 \ \%) & 0.5 \text{ cc} \\ & \text{H}_2 \text{O to make} & 600 \text{ cc} \end{array}$ 

# Solution 7

AgNO<sub>3</sub> 120 g

H<sub>2</sub>O to make 600 cc

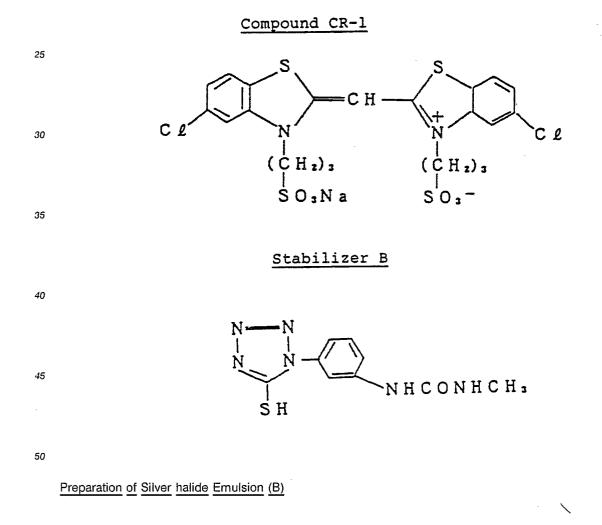
5

Solution 1 was heated to a temperature of 76 °C. Solution 2 and Solution 3 were then added to Solution 1.

Solution 4 and Solution 5 were then added to the mixture at the same time in 10 minutes.

After 10 minutes passed, Solution 6 and 7 were then added to the mixture at the same time in 35 no minutes. After 5 minutes passed, the temperature of the mixture was lowered. The solution was then desalted. Water and gelatin were added to the solution to adjust the pH value thereof to 6.3. As a result, a monodisperse emulsion of cubic particulate silver chloride having an average particle size of 1.1 μm and a particle size fluctuation coefficient of 0.10 (value obtained by dividing standar deviation by average particle size: s.d).

- The emulsion thus obtained was then halved. 12.6 cc of a 0.6 % solution of a blue spectral sensitizing dye (general formula CR-1 shown below) as CR compound was added to one of the two halves of the emulsion. An emulsion of ultrafine particulate AgBr having a particle size of 0.05 μm was added to the emulsion in a proportion of 0.5 mot % based on the host AgCt emulsion. The emulsion was then subjected to mixing and ripening at a temperature of 58 °C for 10 minutes. The emulsion was then subjected to optimum chemical sensitization with sodium thiosulfate. A stabilizer of the undermentioned
- general formula B was added to the emulsion in an amount of 10<sup>-4</sup> mot/mot Ag to prepare Emulsion (A).



# Solution 8

H<sub>2</sub>O 1,000 m t 5 NaC t 3.3 g Gelatin 32 g

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Solution 9

Sulfuric acid (1 N) 24 m t

Solution 10

20 Compound A (Emulsion A) (1 %) 3 mt

# Solution 11

25 NaCł 11.00 g H<sub>2</sub>O to make 200 mł

30

# Solution 12

35 AgNO<sub>3</sub> 32.00 g H<sub>2</sub>O to make 200 m t

40 Solution 13

NaCt 44.00 g K<sub>2</sub>IrCt<sub>6</sub> (0.001 %) 2.3 mt 45 H<sub>2</sub>O to make 560 mt

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#### Solution 14

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AgNO<sub>3</sub> 128 g H<sub>2</sub>O to make 560 m £

Solution 8 was heated to a temperature of 52 °C. Solution 9 and Solution 10 were then added to Solution 8 thus heated. Solution 11 and Solution 12 were then added to the mixture at the same time in 14 minutes. After 10 minutes passed, Solution 13 and Solution 14 were then added to the mixture at the same time in 15 minutes. After 5 minutes passed, the temperature of the emulsion was lowered. The emulsion was then desalted.

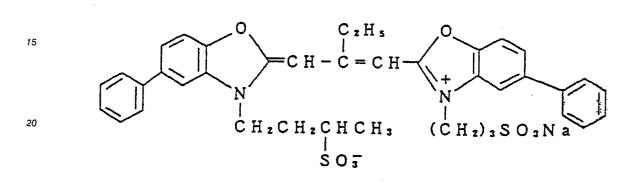
Water and dispersed gelatin were then added to the emulsion to adjust the pH value thereof to 6.2 to obtain a monodisperse emulsion of cubic particulate silver chloride having an average particle size of 0.48  $\mu$ m and a particle size fluctuation coefficient (value obtained by dividing standard deviation by average particle size: s d) of 0.10. A compound of the undermentioned general formula CR-2 was then added to the emulsion in an amount of 4.0 x 10<sup>-4</sup> moll per 1 moll of silver halide. An emulsion of ultrafine particulate

silver bromide having a particle size of 0.05 µm was then added to the emulsion in an amount of 1 mol % as calculated in terms of amount of silver bromide based on the silver silver chloride emulsion. The

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# emulsion was then ripened at a temperature of 58 °C for 10 minutes. Compound CR-2



<sup>25</sup> The emulsion was then subjected to optimum chemical sensitization with sodium thiosulfate at a temperature of 58 °C. The emulsion was further subjected to spectral sensitization with Compound CR-2 added in an amount of  $4 \times 10^{-4}$  mot per 1 mot of silver halide. As a stabilizer Compound B as used in Emulsion A was added to the emulsion in an amount of  $5 \times 10^{-4}$  mot per 1 mot of silver halide.

A Macbeth chart was then photographed on Specimen 102 in the same manner as in Example 1 to prepare a color negative film.

The images on the color negative film were then printed on the color printing light-sensitive material specimens 201 and 202 by means of a printer, and then subjected to the above described color development to obtain color prints.

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 $E_b(\lambda)$ ,  $E_g(\lambda)$  and  $E_r(\lambda)$  of these color prints were determined in the same manner as in Example 1. The results show that Specimen 201 gives the similar characteristics as shown in Fig. 1-(a).  $E_b(\lambda)$ ,  $E_g(\lambda)$  and  $E_r(\lambda)$  obtained from Specimen 202 are shown in Fig. 3-(a).

The images on the color negative film were then printed on Specimen 201 with a filter having a half value width of 30 mm (about 480 to 510 nm) in the similar waveform as shown in Fig. 1-(d) clamped by infrared absorbing filters and interposed between the light source and the negative film, and then subjected

<sup>40</sup> to the similar development. The results of  $E_b(\lambda)$  and  $E_g(\lambda)$  are shown in Fig. 4-(a). The results show that  $E_r$ -( $\lambda$ ),  $E_g(\lambda)$  and  $E_b(\lambda)$  are all independent.

The characteristics concerning the effective spectral sensitivity distribution in the various layers shown in Figs. 3-(a) and 4-(a) are shown in Table 2.

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Table 2

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E (入)	Fig. 3-(a)	E <sub>b</sub> (入)	Fig. 4-(a) E <sub>b</sub> (L)
)		E <sub>g</sub> (人)	$E_{g}(\lambda)$
		$E_r(\lambda)$	E <sub>2</sub> ()
$\max_{E_{g}}(\lambda)/E_{b}(\lambda)$	at 400-485nm 0	.2	0.09
$E_r(\lambda)/E_b(\lambda)$	at 400- 0	.01 >	0.01 >
485 nm max max E <sub>b</sub> (λ)/E <sub>g</sub> (λ)	at 485-570nm 0	.14	0.06
	at 485- 0		0.01 >
max max	at 570-750nm 0 at 570- 0		0.01 > 0.01 >
$E_g(\lambda)/E_r(\lambda)$		.01 /	
$\frac{750 \text{ nm}}{\text{E}_{g}/\text{E}_{b}}$ at 400-	485 nm 0	.03	0.03
$E_r/E_b$ at 400-		.01 >	0.01 >
<sup>5</sup> E <sub>b</sub> /E <sub>g</sub> at 400-	485 nm 0	.02	0.01 >
$E_r/E_q$ at 485-		0.01 >	0.01 >
$E_{\rm b}/E_{\rm r}$ at 570-		).01 >	0.01 >
$\frac{E_q/E_r}{E_q/E_r} = \frac{570}{2}$		).01 >	0.01 >

An object comprising natural green leaves and yellow chrysanthem flowers was then photographed on the color negative light-sensitive material specimen 102 with natural light. The specimen was subjected to the above described development to obtain a color negative film.

The images on the color negative film were then printed on Specimens 201 and 202 (Specimens I and II in Table 3).

On the other hand, the images on the color negative film were printed on Specimen 202 with a multilayer dielectric-deposited film applied in the same manner as described above (Specimen III). The specimen was then subjected to the above described development to obtain a color print. The results are shown in Table 3. The results show that improvements can be seen particularly in saturation and brightness of yellow of the chrysanthem flowers and green of the plant as viewed against the light.

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Object		hrysanthem	Green leaves	s Representat
Specimen used Specimen I S	flower Saturation	Brightness	Saturation	•
Specimen 202		-		
+	Δ	Δ	Δ	X
Specimen 201				
Specimen II				Point II
Specimen 202	0	$\frown$	$\bigcirc$	
+	0	U	U	Δ
Specimen 202		<u></u>	<u> </u>	
Specimen III				Point
Specimen 202			ž	
+ -	$\bigcirc$	0	Ø	$\bigcirc$
Specimen 202	$\smile$	-	-	Ŭ
+				
Filter	<del></del>			

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Fig. 5-(a) shows the representation of the color prints obtained from Specimens II and III and CIE (L \* a \* b) color specification system (as described in Nihon Shikisai Gakkai, "Shikisai Kagaku Handbook, 5th ed., 1985, pp. 140-141) (represented at points II and III, respectively).

Improvements can be seen in saturation and brightness of green and yellow. In particular, color stain of magenta dye is remarkably decreased, and the fidelity in color reproduction is improved.

<sup>50</sup> Furthermore, the use of a filter having a spectral absorption in a wavelength band of 380 to 400 nm gives some improvement in brightness.

#### EXAMPLE 3

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Examples of the measurement of the value of color stain degree  $\beta$ -i and average color mixing degree r of the various Macbeth charts of the present invention will be described hereinafter.

Macbeth charts were photographed with Fuji Photo Film Co., Ltd.'s photographing color light-sensitive material SUPER HR 100 under a photographing standard light source (about 5,500 <sup>°</sup>K). The light-sensitive material was then subjected to development with Fuji Photo Film Co., Ltd.'s standard developing solution CN-16 (Fuji color negative process and chemicals) to obtain a color negative film.

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The images on the color negative film were then printed on Fuji Photo Film Co., Ltd.'s color photographic paper SUPER HR Paper by means of a printer (see P curve in Fig. 1-(b)). The color photographic paper thus printed was then subjected to development with Fuji Photo Film Co., Ltd.'s standard developing solution CP-20 (Fuji color negative process and chemicals) to obtain a color print.

The spectral sensitivity of GL in the color photographic paper used in the present example was determined by a conventional method. (See GL curve in Fig. 1-(b))

The color stain degree  $\beta_i$  of color of Macbeth chart i was determined. The results are shown in Table 4. The results show that when i is 16 (Y), the highest color stain degree is obtained, and the next highest color stain degree is obtained at i = 11 (YG) and i = 12 (OY). Accordingly, the color mixing degree of the print thus, obtained at i = 16 Y is 0.47. The average color mixing degree r of GL was determined by means of the equation (2-5) to obtain 0.14.

A multilayer dielectric-deposted filter was prepared. The spectral transmittance F ( $\lambda$ ) curve of the filter thus obtained is shown in Fig. 1-(d). For the color chart i, the exposure is given by the following equation:

 $E i = \begin{cases} 570 \\ S(\lambda) \cdot T i(\lambda) \cdot P(\lambda) \cdot F(\lambda) d\lambda \\ 485 \end{cases}$ 

The value of color stain degree  $\beta$ -i<sup>F</sup> obtained with the filter interposed between the light source and GL in the printing light-sensitive material during the printing is shown in Table 4. When i is 16 (Y), the color mixing degree degree  $\beta$ -i<sup>F</sup> is 0.23 and the average color mixing degree r<sup>F</sup> of GL is 0.07. Thus, it was found that the multilayer dielectric-deposited filter halves the color of GL in a color printing material.

Furthermore, printing was conducted with a filter  $F^{\circ}$  (spectral transmittance  $F^{\circ}$  ( $\lambda$ ); see Fig. 2-(d)) in the same manner as described above. If the same light-sensitive material and color development process as described are used, the value of the average color stain degree  $r^{F^{\circ}}$  of GL is in the range of 0.02 to 0.03.

In general, the color mixing degree of a color printing light-sensitive material shows the greatest value in GL. Therefore, it can be said that the above described value is the color mixing degree of the color printing light-sensitive material.

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TAB	LE	4
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5	i	Name of color	Ηi <sup>ο</sup>	Hi	αi	βi	βi <sup>r</sup>
	1		1.75	1.78	1.02	0.02	0.02
10	2		0.82	0.87	1.07	0.07	0.03
	3		0.98	0.93	0.94	-0.06	-0.03
	4		1.03	1.16	1.12	0.12	0.06
15	5		0.97	0.92	0.95	-0.05	-0.02
	6	BG	0.50	0.53	1.06	0.06	-0.02
20	7	0	0.96	1.19	1.23	0.23	• 0.12
	8		1.48	1.29	0.87	-0.13	-0.06
	9	M. R	1.66	1.64	0.99	-0.01	0
25	10	P	2.10	1.86	0.89	-0.11	-0.05
	11	YG	0.43	0.59	1.37	0.37	0.18
30	12	0. Y.	0.55	0.74	1.35	0.35	0.17
	13	В	2.04	1.69	0.83	-0.17	-0.08
	14	G	0.60	0.73	1.20	0.20	0.10
35	15	R	2.26	2.30	1.02	0.02	0.02
	16	Y	0.40	0.59	1.47	0.47	0.23
40	17	М	1.56	1.43	0.92	-0.08	-0.03
	18	С	0.85	0.80	0.95	-0.05	-0.03
45	22	Grey	1.0	1.0	1.0	0	0

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EXAMPLE 4

#### Preparation of multilayer color printing light-sensitive material

A multilayer color photographic paper was prepared by coating various layers of the undermentioned composition on a paper support laminated with polyethylene on both sides thereof. The coating solution used were prepared according to the procedure in Example 2, to prepare Specimen 401. 5

## Preparation of Specimens 402 to 403

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Specimen 402 was prepared in the same manner as in Specimen 301 except in that the compound of the general formula D-3 was further incorporated in the 4th layer. Specimen 403 was prepared in the same manner as in Specimen 402 except in that Compound (D-3) to be incorporated in the 4th layer was replaced Compound (S-1) and a functional dye (F-1) as is shown in Table 5. Compounds (S-1) and (F-1) were dispersed in the layer together with an ultraviolet absorber. Compound (D-3) was incorporated in the layer in the form of an aqueous solution. 15

# TABLE 5

5	Specimen	Compound incorp in the 3rd 1a		ompound incorporated in the 4th layer	
	401	(D-1) 1.4 x 10	$-4 mol/m^2$	-	
10	402	11	(D-	3) $1.4 \times 10^{-4} \text{ mol/m}^2$	
	403	"	(S-)	1) 0.20 g/m <sup>2</sup>	
			(F-)	1) $1 \times 10^{-4} \text{ mol/m}^2$	
15			•		
20	(	0 1)			
	(S-1)				
			OH 		
25			SO 3 Na		
		(n) H <sub>31</sub> C <sub>15</sub>			
30		1	l DH -		
	(	F — 1 )	~		
	ζ.	0	H <sub>3</sub> C		
35	(CH <sub>3</sub> ) <sub>3</sub>	· · · · · · · · · · · · · · · · · · ·	СН	CH2CH2SO3Na	
		0 NO	N L	- CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> Na	
40	0 z				
45		SO <sub>z</sub> N CH <sub>3</sub>			
40		SU2N C16H33	Ś0₃Na		

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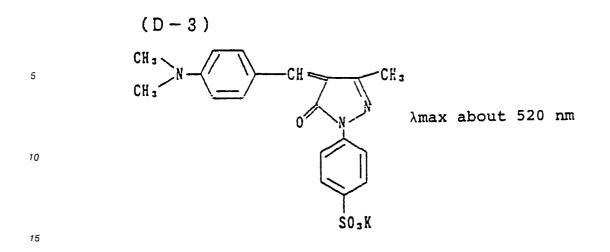
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The color printing light-sensitive material thus obtained was subjected to the following color development.

20	Processing step	Temperature	Time
	Color development	35 °C	45 sec.
25	Blix	30-36 °C	45 sec.
	Stabilization 1	30-37 °C	20 sec.
	Stabilization 2	30-37 °C	20 sec.
30	Stabilization 3	30-37 °C	20 sec.
	Stabilization 4	30-37 °C	30 sec.
35	Drying	70-85 °C	60 sec.

(The stabilizing step was effected in a countercurrent process in which water flows from the tank 4 to the tank 1 through the tank 3 and the tank 2.)

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The composition of the various processing solutions used were as follows:

# Color developing solution

	Water 800 m		
	Ethylenediaminetetraacetic acid 2.0 g		
	Triethanol amine 8.0 g		
50	Ammonium sodium chloride 1.4 g		
	Disodium ethylenediaminetetraacetate 3 g		
	Potassium carbonate 25 g		
	N-ethyl-N-( <i>β</i> -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate		
	N,N-diethylhydroxylamine 4.2 g		
55	5,6-Dihydroxybenzene-1,2,4-trisulfonic acid 0.3 g		

Fluorescent brightening agent (4,4<sup>'</sup>-diaminostylbene series) 2.0 g Water to make 1,000 m t pH at 25  $^{\circ}$ C 10.10

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#### Blix solution

Water 400 m t
 Ammonium thiosulfate (70 %) 100 m t
 Sodium sulfate 18 g
 Ferric ethylenediaminetetraacetate (III) 55 g
 Glacial acetic acid 8 g
 Water to make 1,000 m t

pH at 25 °C 5.5

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#### Stabilizing solution

Formalin (37 %) 0.1 g Formalin-sulfite addition product 0.7 g 25 5-Chloro-2-methyl-isothiazoline-3-one 0.02 g 2-Methyl-4-isothiazoline-3-one 0.01 g Copper sulfate 0.005 g Water to make 1,000 m t pH at 25 °C 4.0

30 Specimens 401 to 403 thus obtained were than processed in the same manner as in Example 3 with the color negative film shown in Example 3 as a color print original to obtain a color mixing degree  $\beta \cdot i = 15$  and an average color mixing degree r (Y, i = 16). The results are shown in Table 6.

The results show that Specimens 402 and 403 exhibit an excellent color reproducibility.

35	TABLE 6				
	Specimen	Name of color	<u> </u>	r	
	401 (Comparative)	16 Y	0.47	0.14	
40	402	16 Y	0.46	0.12	
	403	16 Y	0.40	0.11	
45	404	16 Y	0.38	0.10	

50

#### EXAMPLE 5

Specimen 404 was prepared in the same manner as in Specimen 403 except in that the silver halide emulsion (Br: 80 mol%) to be incorporated in the 1st layer was replaced by the silver halide emulsion A (Br: 0.5 mol%) used in Example 2 and the silver halide emulsion B (Br: 1.0 mol%) used in Example 2 was incorporated in the 3rd layer.

In the same manner as in Specimen 403 in Example 4, the color mixing degree  $\beta i = 16$  and the average color mixing degree r of Specimen 104 were determined. The results are shown in Table 6. The results show that distinction between orange yellow and lemon yellow and the reproduction of sharp green are improved.

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#### EXAMPLE 6

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#### Preparation of photographing color light-sensitive material

A multilayer color light-sensitive material specimen 601 was prepared by coating various layers of 5 Example 1 or an undercoated cellulose triacetate film support in the same manner as in Example 1.

#### Preparation of Specimen 602

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Specimen 602 was prepared in the same manner as in Specimen 601 except in that the yellow colloidal silver to be incorporated in the 10th layer was replaced by Compound C shown below as a comparative compound in an amount of 0.2 g.

Compound C

<sup>30</sup> CH<sub>3</sub>SO<sub>2</sub>NH 
$$C = CH$$
  $NC$   $C = CH$   $N$   $CH_2COOC_4H_{\bullet}(n)$ .  
CH<sub>3</sub>SO<sub>2</sub>NH  $C$   $CH_3$   $CH_2COOC_4H_{\bullet}(n)$ 

(Yellow dye as described in Japanese Patent Application (OPI) No. 205,934/86)

Color development of photographing color light-sensitive material was carried out according to the same procedure as in Example 1.

Color negative films were prepared in the same manner as in Example 3 except in that the color lightsensitive material for use in photographing was replaced by Specimens 601 and 602. These color negative films were then used as print originals.

The images on these print originals were then printed on Specimen 404 of Example 5 as a printing light-sensitive material with the multilayer dielectric-deposited filter of Example 3 mounted in Fuji Photo Film Co., Ltd.'s automatic color printer Type FAP-3500 to obtain color prints. The results are shown in Table 7.

45	TABLE 7				
	Specimen	<u>    i    </u>	Name of color	β <sub>i</sub>	<u> </u>
50	601	16	Y	0.25	0.09
	602	16	Y	0.22	0.07

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When a color negative light-sensitive material comprising a filter layer was used in combination with the above described filter, the average color mixing degree was further lowered, attaining an excellent color reproducibility.

# EXAMPLE 7

A photographing multilayer color light-sensitive material specimen 701 was prepared by coating various s layers of the undermentioned compositions on an under-coated cellulose triacetate film support.

## Preparation of color light-sensitive material for use in photographing

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## Composition of light-sensitive layer

The value of the coated amount of each component is represented in g/m<sup>2</sup>. The coated amount of silver halide is represented in terms of amount of silver. The coated amount of sensitizing dye is represented by molar amount thereof per 1 mot of silver halide contained in the same layer.

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## Specimen 701

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# 1st layer (antihalation layer)

Black colloidal silver 0.18 Gelatin 0.40

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2nd layer (intermediate layer)

35 2,5-Di-t-pentadecyl hydroquinone 0.18 EX-1 0.07 EX-3 0.02 EX-12 0.002 U-1 0.06 U-2 0.08 40 0.10 U-3 HBS-1 0.10 HBS-2 0.02 Gelatin 1.04

45

3rd layer (1st red-sensitive emulsion layer)

50 Monodisperse emulsion of silver bromoiodide (Agl content: 6 mot %; average particle diameter: 0.6 μm; coefficient of fluctuation in particle diameter: 0.15) 0.55

HBS-1	0.005
EX-10	0.020
Gelatin	1.20

## 4th layer (2nd red-sensitive emulsion layer)

Emulsion of tabular particulate silver bromoiodide (Agl content: 10 mot %; average particle diameter: 0.7  $\mu$ m; average aspect ratio: 5.5; average thickness: 0.2  $\mu$ m) 1.0

Sensitiz	zing dye I	5.1 x 10 <sup>-5</sup>
Sensitiz	zing dye II	1.4 x 10 <sup>-5</sup>
Sensitiz	zing dye III	2.3 x 10 <sup>₄</sup>
Sensitiz	zing dye IV	3.0 x 10 <sup>-5</sup>
EX-2	0.400	
EX-3	0.050	
EX-10	0.015	
Gelatin	1.30	

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5th layer (3rd red-sensitive emulsion layer)

Silver bromoiodide emulsion (Agl content: 16 mot %; average particle diameter : 1.1 µm) 1.60

25	Sensitizir	ng dye IX	5.4 x 10 <sup>−5</sup>
	Sensitizir	ng dye ll	1.4 x 10 <sup>−5</sup>
	Sensitizir	ng dye III	2.4 x 10 <sup>−4</sup>
	Sensitizi	ng dye IV	3.1 x 10 <sup>-5</sup>
	EX-3	0.240	
30	EX-4	0.120	
	HBS-1	0.22	
	HBS-2	0.10	
	Gelatin	1.63	

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6th layer (intermediate layer)

	EX-5	0.040
40	HBS-1	0.020
	EX-12	0.004
	Gelatin	0.80

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7th layer (1st green-sensitive emulsion layer)

Emulsion of tabular particulate silver bromoiodide (Agl content: 6 mol %; average particle diameter: 0.6 µm; average aspect ratio: 6.0; average thickness: 0.15) 0.40

50	Sensitizi	ng dye V	3.0 x 10 <sup>-5</sup>
	Sensitizi	ng dye VI	1.0 x 10 <sup>−</sup>
	Sensitizi	ng dye VII	3.8 x 10 <sup>−₄</sup>
	EX-6	0.260	
	EX-1	0.021	
55	EX-7	0.030	
	EX-8	0.025	

HBS-1	0.100
HBS-4	0.010
Gelatin	0.75

## 8th layer (2nd green-sensitive emulsion layer)

Monodisperse emulsion of silver bromoiodide (Agl content: 9 mo t %; average particle diameter: 0.7 μm; 10 coefficient of fluctuation in particle diameter: 0.18) 0.80

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	Sensitiz	ing dye V	2.1 x 10 <sup>-5</sup>
	Sensitizi	ing dye VI	7.0 x 10 <sup>-5</sup>
	Sensitizi	ing dye VII	2.5 x 10 <sup>−₄</sup>
	EX-6	0.180	
15	EX-8	0.010	
	EX-1	0.008	
	EX-7	0.012	
	HBS-1	0.160	
	HBS-4	0.008	
20	Gelatin	1.10	

9th layer (3rd green-sensitive emulsion layer

25

#### Silver bromoiodide emulsion (Agl content: 12 mot %; average particle diameter:1.0 $\mu$ m) 0.77 3.5 x 10<sup>-5</sup> Sensitizing dye V 8.0 x 10<sup>-5</sup> Sensitizing dye VI Sensitizing dye VII $3.0 \times 10^{-4}$ 0.065 EX-6 30 EX-11 0.030 EX-1 0.025 0.25 HBS-1 HBS-2 0.10 Gelatin 1.74 35

<u>10th layer (yellow filter layer)</u> Yellow colloidal silver 0.

Yellow colloidal silver0.05EX-50.08HBS-30.03Gelatin0.95

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11th layer (1st blue-sensitive emulsion layer)

- 50 Emulsion of tabular particulate silver bromoiodide (Agl content: 6 mo t %; average particle diameter: 0.6 μm; average aspect ratio: 5.7; average thickness: 0.15 μm)
   0.24 Sensitizing dve VIII
   3.5 x 10<sup>-4</sup>
  - Sensitizing dye VIII
     3.5

     EX-9
     0.85

     EX-8
     0.12

     HBS-1
     0.28
- Gelatin 1.28

# 12th layer (2nd blue-sensitive emulsion layer)

Monodisperse emulsion of silver bromoiodide (Agl content: 10 mot %; average particle diameter : 0.8  $\mu$ m; coefficient of fluctuation in particle diameter: 0.16) 0.45

5 Sensitizing dye VIII 2.1 x 10<sup>-4</sup>

# 13th layer (3rd blue-sensitive emulsion layer)

10

- Silver bromoiodide emulsion (Agl content: 14 mo t %; average particle diameter: 1.3 μm) 0.77 Sensitizing dye VIII 2.2 x 10<sup>-4</sup> EX-9 0.20 HBS-1 0.07
- 15 Gelatin 0.69

20

# 14th layer (1st protective layer)

Silver bromoiodide emulsion (Agl content: 1 mot %; average particle diameter: 0.07 μm)0.5U-40.11U-50.17HBS-10.90Gelatin1.00

15th layer (2nd protective layer)

30

25

Particulate polymethyl acrylate (particle diameter: about 1.5  $\mu$ m) 0.54

S-1 0.15

S-2 0.05

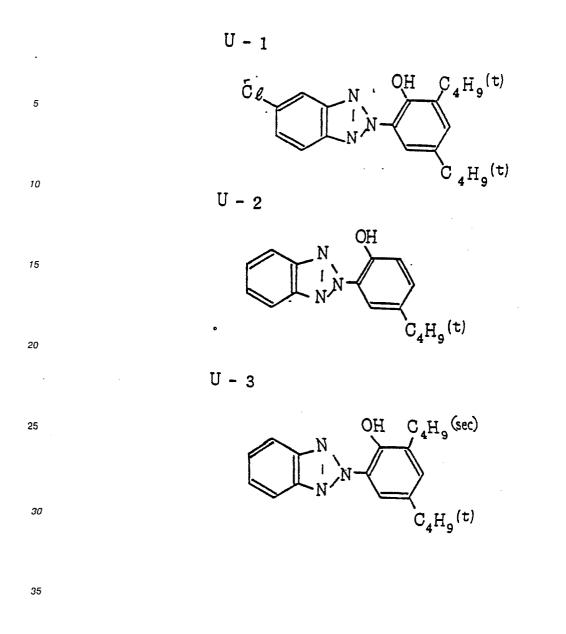
Gelatin 0.72

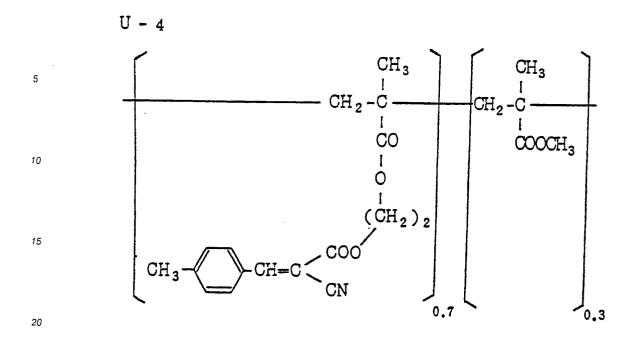
<sup>35</sup> Besides the above described components, a gelatin hardener H-1 and a surface active agent were incorporated in each layer.

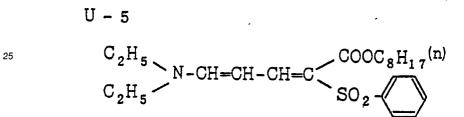
40

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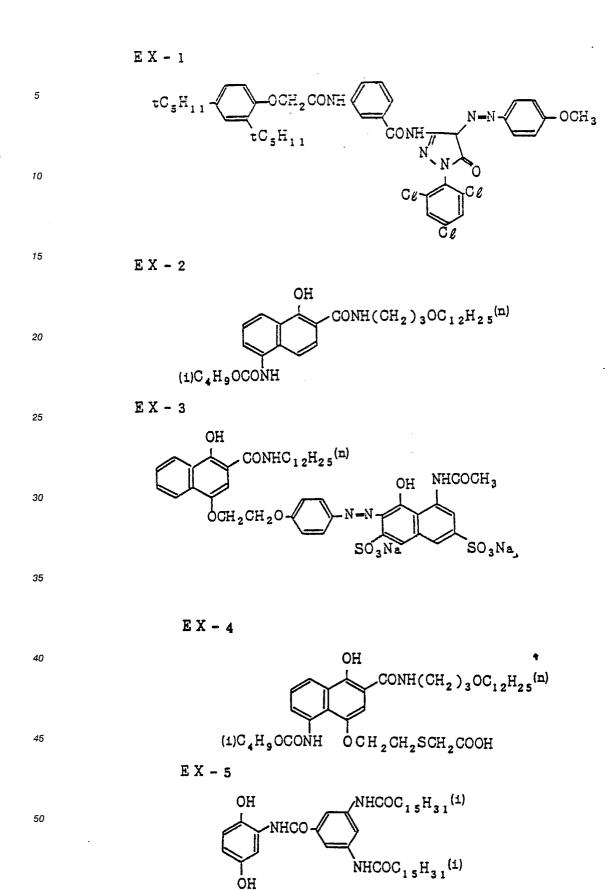


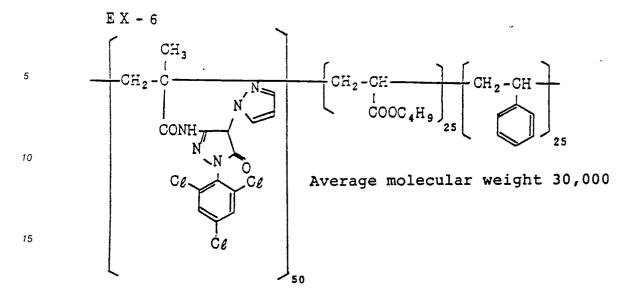






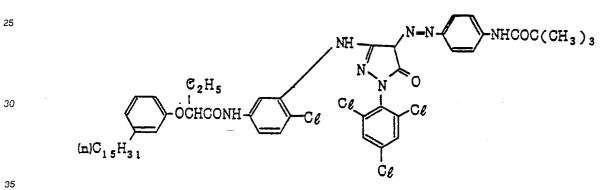
55 .



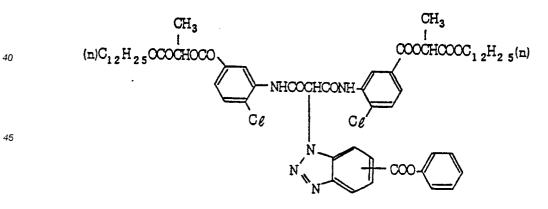


20

EX-7

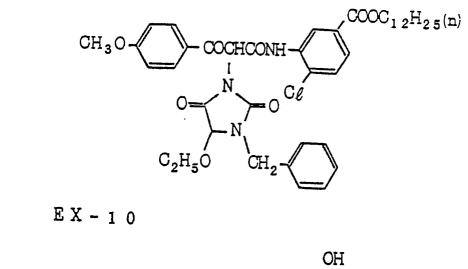


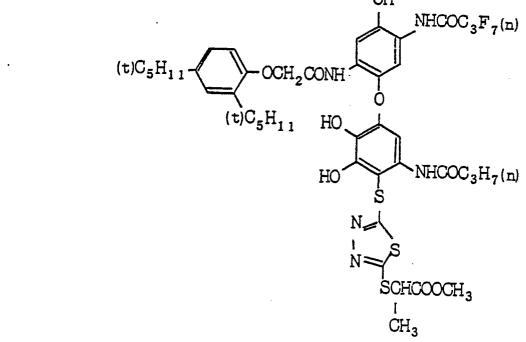
E X - 8



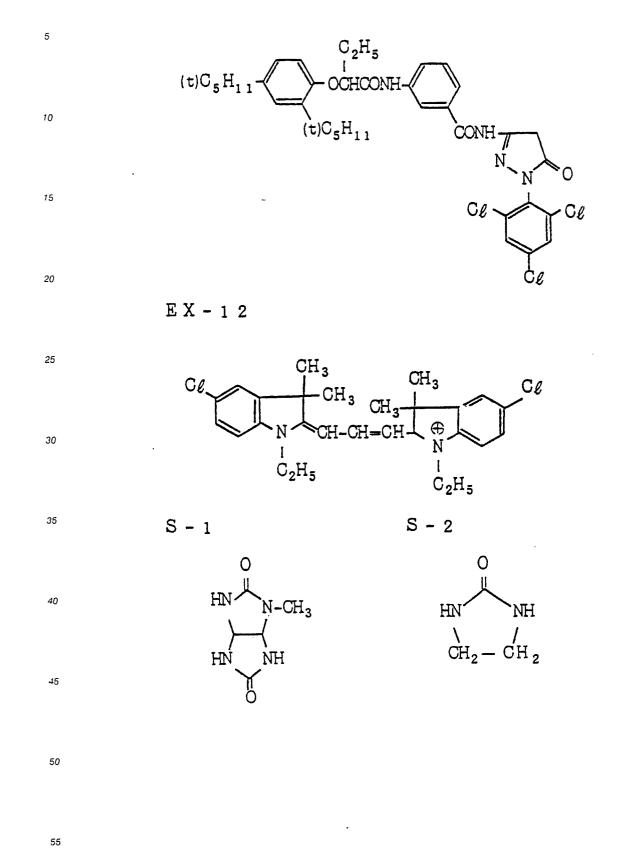
50

EX-9

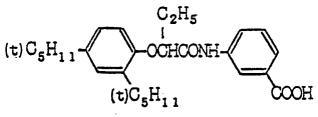




EX-11

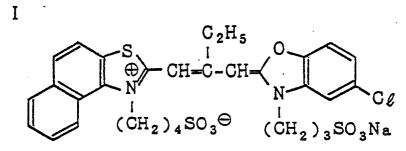


HBS-1: Tricresyl phosphate HBS-2: Dibutyl phthalate HBS-3: Bis(2-ethylexyl)phthalate HBS-4



H - 1  $CH_2 = CH - SO_2 - CH_2 CONH - CH_2$  $CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$ 

Sensitizing dye



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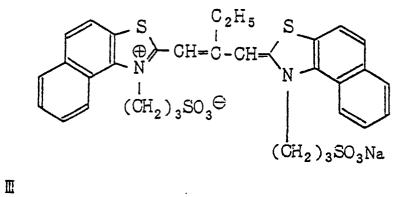
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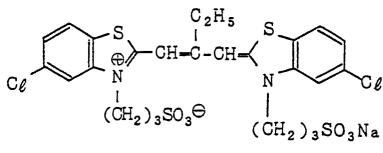
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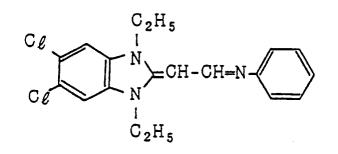






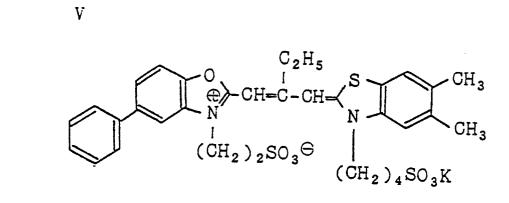


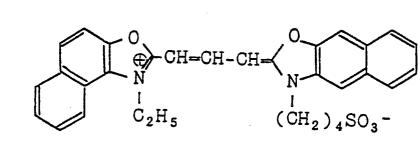






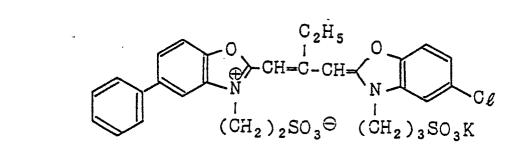
-

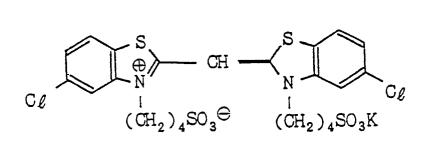




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 $\begin{array}{c}
 S & 1 \\
 \oplus & -CH=C-CH= \\
 N \\
 & (CH_2)_3 SO_3 \\
 & (CH_2)_4 SO_3 Na
\end{array}$ 

Specimens 702 and 703 were prepared in the same manner as in Specimen 701 except in that EX-6 was replaced by VII-(2) and X-(7) was used as shown in Table 8. (EX-2, EX-4 and EX-7 are couplers according to the present invention.)

			TABLE 8			
		Specimen	702	Specime	en 703	
	7th layer	VIII-(2)	0.25			
,	8th layer	VIII-(2)	0.20	"		
	9th layer	VIII-(2)	0.08	11		
	llth layer		-	EX-9	0.40	
i				X-(7)	0.50	
	12th layer		-	EX-9	0.10	
)				X-(7)	0.10	

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An object comprising a Macbeth grey color chart (No. 22) and a fresh flower (e.g. a chrysanthemum or palm leaf) was photographed on these light-sensitive material specimens by means of a light source having <sup>55</sup> a color temperature of about 5,400 °K.

These specimens were then subjected to the following color development to obtain color negative films (print originals).

Color development of color light-sensitive material for use in photographing is carried out according to

the same procedure as in Example 1.

## EXAMPLE 8

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## Preparation of multilayer color printing light-sensitive material

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A multilayer color photographic paper specimen 801 was prepared by coating various layers of the undermentioned compositions on a paper support laminated with polyethylene on both sides thereof.

### 15 Preparation of 1st layer coating solution

19.1 g of a yellow coupler (ExY) and 4.4 g of a dye stabilizer (Cpd-1) were dissolved in 27.2 cc of ethyl acetate and 7.7 cc of a solvent (Solv-1). The solution thus obtained was then emulsion-dispersed in 18.5 cc of a 10% aqueous solution of gelatin containing 8 cc of 10% sodium dodecylbenzenesulfonate. On the other hand, a blue-sensitive sensitizing dye of the undermentioned general formula was added to a silver bromochloride emulsion (containing 80.0 mot% of silver bromide and 70 g/kg of Ag) in an amount of 5.0 x 10<sup>-4</sup> mot per 1 mot of silver. The emulsion dispersion and the emulsion thus obtained were mixed to prepare the 1st layer coating solution having the undermentioned composition. The coating solutions for the 2nd layer to the 7th layer were similarly prepared. As a gelatin hardener for each layer there was used sodium 1-oxy-3,5-dichloro-s-triazine.

As sensitizing dyes for the various layers there were used the following compounds.

## Blue-sensitive emulsion layer

Compound I-(1) (5.0 x  $10^{-4}$  mot per 1 mot of silver halide)

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## Green-sensitive emulsion layer

40 Compound III-(9)  $(4.0 \times 10^{-4} \text{ mol per 1 mol of silver halide});$ and Compound III-(8)  $(7.0 \times 10^{-5} \text{ mol per 1 mol of silver halide})$ 

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## Red-sensitive emulsion layer

Compound IV-(8)  $(0.9 \times 10^{-4} \text{ mol per 1 mol of silver halide})$ 

50 Compound I-(9) was incorporated in the red-sensitive emulsion layer in an amount of 2.6 x 10<sup>-3</sup> mol per 1 mol of silver halide.

1-(5-Methylureidephenyl)-5-mercaptotetrazole was incorporated in the blue-sensitive emulsion layer, the green-sensitive emulsion layer and the red-sensitive emulsion layer in amounts of 4.0 x  $10^{-6}$  mot, 3.0 x  $10^{-5}$  mot and 1.0 x  $10^{-5}$  mot per 1 mot of silver halide, respectively.

4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene was incorporated in the blue-sensitive emulsion layer and

the green-sensitive emulsion layer in amounts of  $1.2 \times 10^{-2}$  mol and  $1.1 \times 10^{-2}$  mol per 1 mol of silver halide, respectively.

For the purpose of inhibiting irradiation, the dyes used in Example 2 were incorporated in the emulsion layer.

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#### Layer construction

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The composition of the various layers is the same as in Example 2. Specimen 802 was prepared in the same manner as in Specimen 801 except in that the silver halide emulsion (Br: 80 mot%) to be incorporated in the 1st layer was replaced by the silver halide emulsion A (Br: 0.5 mot%) used in Example 2 shown below and the undermentioned silver halide emulsion B used in

- Example 2 (Br: 1.0 mot %) was incorporated in the 3rd layer.
- <sup>15</sup> ExY, ExM or ExC as used in Example 8 is a suitable color coupler which can be used in the present invention. Specimens 801 and 802 were then exposed to light by means of a spectral photographing machine which had been corrected so as to give the same spectral energy intensity of the light source. These specimens were then subjected to the same color development as in Example 2, except for adjusting pH value of blix being 5.5.
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The results thus obtained are shown in Figure 1-(c). Curve 1 was obtained from Specimen 801, and Curve 2 was obtained from Specimen 802. J indicates the maximum spectral sensitivity showing the characteristics of a J type spectral sensitization and an M type sensitization.

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## EXAMPLE 9

The images on the color negative films obtained from Specimens 701 and 702 in Example 7 were then printed on Specimen 801 and Specimen 802 by means of Fuji Photo Film Co., Ltd.'s Autoprinter Type FAP-30 35000. These specimens were then subjected to the following color development B.

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5	Processing step	Temp.	Time		Supply amount*	Tank Volume
J	Color development	38°C	1 min. 40	sec.	290 ml	17 L
10	Blix	33°C	40	sec.	100 m <sup>l</sup>	9 L
	Rinse 1	30-34°C	15	sec.	-	4 L
	Rinse 2	87	"		-	4 L
15	Rinse 3	"	11		Shown in Table 9	4 L
	Drying	70-80°C	50	sec.		
20	* Valu	e per 1 m	<sup>2</sup> of light-	-sensi	tive mater:	ial
	(The	rinse wa	s effected	in a c	countercur	rent
25	pro	cess in w	hich water	flows	from the	tank 3
	to	the tank	l through t	the tar	nk 2.)	
			solution o	carried	l over from	n the
30	pre-	bath was	30 m²/m².)			

# Color development B

The composition of the processing solutions used in the various steps were as follows:

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# Color developing solution

5		Tank solution	Supply liquid
	Water	800 ml	800 ml
10	Diethylenetriaminepenta- acetic acid	1.0 g	1.0 g
	Nitrotriacetic 1-hydroxy- ethylidene-1,l-diphosphonic acid	2.0 g	2.0 g
<i>i</i> 5	Potassium bromide	0.5 g	-
	Potassium Carbonate	30 g	30 g
20	N-ethyl-N-(β-methanesulfon- amideethyl)-3-methyl-4-amino- aniline sulfate	5.5 g	7.5 g
25	N,N-diethylhydroxylamine	3.6 g	5.5 g
25	Fluorescent brightening agent	1.5 g	2.0 g
30	Triethylenediamine(1,4-diaza- bicyclo[2,2,2]octane	5.0 g	5.0 g
30	Water to make	1,000 ml	1,000 ml
	pH at 25°C	10.20	10.060

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# Blix solution

40		Tank solution	Supply liquid
	Water	400 m <sup>l</sup>	400 m <sup>l</sup>
45	Ammonium thiosulfate (70%)	200 m <sup>g</sup>	300 m <sup>g</sup>
	Sodium sulfite	20 g	40 g
50	Ferric ammonium ethylenediamine tetraacetate	e- 60 g	120 g
	Disodium ethylenediaminetetra- acetate	5 g	10 g

Tank	Supply
solution	liquid

Water to make

# 1,000 mg 1,000 mg

pH at 25°C

10

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# Rinsing solution

Aqueous ammonia and water were used to give a pH as shown in Tables 9-1 and 9-2.

<sup>15</sup> Water which had been passed through an ion exchange resin (calcium and magnesium content: 3 ppm or less each) was used.

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The specimens thus developed were then observed for the degree of stain on the resulting images and background. The results are shown in Table 9-1.

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5 10				Stain	(Poor in cyan color forming)				Specimen 201 (slightly poor desil- vering)					No stain on background (Excellent) Stain observed on background and images
15		Supply amount (m£)	(supply amount/ amount	OVER	0	0	0	0	Q~	∧ ~ x	0	0		o stain on bu tain observed and images
20	αi [	Suppl	(suppl) am	g O	(8)	(8)	(8)	(8)	(8)	(8)	(8)	(8)		No Sta an
25	d results		Presence of fluorescent	origniening agent	240	240	240	240	240	240	240	*2 240		(T)
30	tions and	Rinse	Prese fluor	agent	NO	No	NO	No	NO	NO	No	Yes *		und (Fair) nk, etc.) :)
35	ssing conditions	ce of cent	ening in	DIULION	(3.3)	(4.0)	(2*0)	(0'9)	(7.0)	(6.5)	(2.0)	(2.0)	d/۴)	in on background n (yellow, pink, (Inacceptable)
40	l Proces	Presence of flucrescent	brightening agent in	(Hd) os XIIG	No	NO	NO	No	0 N	NO	Yes *1	NO	amount (2.0	Little stain Color stain observed (I
45 50	TABLE 9-1	Presence of	brightening agent in	developing solution	Yes	Yes	Yes	Yes	Yes	No	No	No	1,2: Used	<pre>     Color stain     x     color stain     observed ( </pre>
55		<u>н</u> , 4	-4 <i>-4</i>	o No.	1	7	n	4	ഗ	9	7	8	*	

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Specimens prepared in the same manner as in Specimens 4, 6, 7 and 8 except in that the fluorescent brightening agent XI-(2) was replaced by XI-(1), XI-(2), XI-(4), XI-(5) or I-(6) were subjected to the same color development. As a result, the similar effect of stain removal was observed.

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5 The processing No. 9 was then effected in the same manner as in the processing No. 3 except in that the fluorescent brightening agent XI-(2) was replaced by Compound A of the following general formula:

Compound A

NaO<sub>3</sub>S(CH<sub>2</sub>)<sub>3</sub>NH

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The processing Nos. 10 and 11 were effected with Compound XI-(10) or a 1 : 1 mixture of Compound XI-(10) and Compound XI-(2). The results are shown in Table 2-2.

	Stain	(Some resi- dual color)			
	ount ount/ id	Q~ ₹	©	0	
nd results	<pre>se Supply amount (m%) (supply amount/ amount carried over</pre>	240 (8)	240 (8)	240 (8)	
Processing conditions and results	Rinse Presence of ( fluorescent brightening agent	NO	NO	No	
9-2 Proces	ence of rescent htening nt in solution pH)	(5.0)	(2.0)	(2.0)	
TABLE	Presence o fluorescen brightenin agent in blix solut (pH)	NO	No	No	
	Presence of fluorescent brightening agent in developing solution	Compound (A)	I-(10)	I-(10) I	I-(2) 1
	No.	6	10	11	

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If a continuous processing (1 m<sup>2</sup> or more) is effected without supplying a blix solution or rinsing solution, an increase in stain is generally observed. However, even in such a condition, the processing Nos. 3, 10 and 11 give a relatively small increase in stain. The most excellent results were obtained.

## EXAMPLE 10

The effective spectral sensitive energy distribution Eb(λ), Eg(λ) or Er(λ) obtained when a grey object was photographed on the color printing light-sensitive materials used in the previous example in combination with the color negative films used in the previous example as shown in Table 10 is shown in Figs. 2-(c), 3-(c), 4-(c) and 5-(c). Fig. 2-(c) shows that in the combination of Specimen 701 and Specimen 701 Er(λ) is independent but Eg(λ) and Eb(λ) are independent. Figs. 3-(c) and 4-(c) show that Er(λ) and Eg(λ) are independent. Fig. 5-(c) shows that Er(λ), Eg(λ) and Eb(λ) are all independent.

5 10		Ελ	Shown in Fig. 2-(c) Shown in Fig. 3-(c)	Shown in Fig. 3-(c) Shown in Fig. 3-(c)
20 25	TABLE 10	Color printing light-sensitive material used	Specimen 801 Specimen 802	Specimen 801 Specimen 802
30		Photographing color light- sensitive material used	Specimen 701 "	Specimen 702 "
45		No.	7 7	w 4.

## EXAMPLE 11

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The images on the color negative films obtained from the photographing color light-sensitive material specimens 701 and 702 of Example 7 were printed on the color printing light-sensitive material specimens 801 and 802 in the same manner as in Example 9. These specimens were then subjected to the color development process B No. 3 to obtain color prints. These specimens were observed by the naked eye for the photographic properties. The results are shown in Table 11. On the other hand, the representation of

green leaf of natural cycad and yellow chrysanthemum flower in CIE (L\* a\* b\*) color specification system (as described in Nihon Shikisai Gakkai, "Shikisai Kagaku Handbook" (5th ed., 1985, pp. 140-141) gave the results show in Figure 6-(c). The results show that saturation and lightness are improved for yellow, particularly for green, and color fidelity is remarkably improved.

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		Fig. 6-(c)	Θ		9	9		
		w Lightness	Δ	0	0	0		
		<u>Yellow</u> Saturation	Δ	0	0	O	Slightly poor	lent
		1 Lightness	Δ × Χ	0	0	0	Δ Sligh	D Excellent
-	TABLE 11	Green Saturation	Φ	0	0	Ô		
		Color printing light- sensitive material used	Specimen 801	Specimen 802	Specimen 801	Specimen 802	X Poor	$\bigcirc \cdots$ Fair
		Color negative film used	Specimen 701	Specimen 701	Specimen 702	Specimen 702		

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On the other hand, these specimens were exposed to light through a sharp cutoff filter I as shown in Fig. 7-(c) (wavelength band longer than 440 nm is cut) or a sharp band stop filter II as shown in Fig. 1-(d) (wavelength band of 490-530 nm is cut; W<sub>1/4</sub>/W<sub>3/4</sub>: 0.67) and then developed in the same manner as described above to obtain color prints. The results are shown in Table 12 and Fig. 6-(c).

10	Color negative film used	Color printing light-sensitive material used	Filter used I		Point in Fig. 6	
15	Specimen 701	Specimen 801	None	None	1	
	"		None	Used	2	
•	11	11	Used	Used	$\overline{\mathbf{O}}$	
20	Specimen 702	Specimen 801	None	None	3	
	17	87	None	Used	4	
25	"	Specimen 802	None	None	5	
20	"	11	Nonè	Used	6	
-		87	Used	Used	(almost	
30			-		corresponds to 6)	

## TABLE 12

<sup>35</sup> Thus, the use of the sharp and band cut-off filter II gives an improvement in the saturation, lightness and hue fidelity of yellow, green and violet color systems.

In particular, the incorporation of a pyrazoloazole coupler represented by the general formula (VIII) in a photographing color light-sensitive material and a color printing light-sensitive material exhibited further improvement in saturation and fidelity of red color system.

<sup>40</sup> E ( $\lambda$ ) of the color printing light-sensitive materials obtained when the filters I and II were used in Table 12 (No. 8) is shown in Fig. 8-(c). Fig. 8-(c) shows that Er ( $\lambda$ ), Eg ( $\lambda$ ) and Eb ( $\lambda$ ) are all independent.

## EXAMPLE 12

Specimen 703 obtained in Example 7 was used to replace Specimen 102 in Examples 10 and 11. As a result, an improvement in color reproducibility was observed similarly.

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## EXAMPLE 13

A polished white glass plate having a thickness of 3 mm was cleaned with soapy water. After being <sup>55</sup> dried, the glass plate was then ultrasonically cleaned in a liquid fleon in an ultrasonic cleaner for 1 minute and 30 seconds. The glass plate thus treated was later used as a substrate for deposited film interference filter. The glass plate was then mounted on a substrate holder in an electron beam heating type evaporator. One of two evaporation sources was provided with 20 g of pelletized silicon oxide and the other was

provided with 20 g of aluminum oxide. The evaporator was pre-evacuated for 10 minutes by a rotary pump, and then evacuated by an oil diffusion pump for 20 minutes so that the pressure therein reached  $2 \times 10^{-5}$  torr. Then, silicon oxide and aluminum oxide were alternately evaporated. The substrate was kept at a temperature of about 350°C by a halogen lamp in the tank during evaporation. Silicon oxide was heated by

an electron beam of 5 KV and 30 mA for 6 minutes, and aluminum oxide was heated by an electron beam of 5 KV and 250 mA for 8 minutes. The thickness of the film thus deposited was controlled while being observed by an optical monitor. In such a manner, Filter Specimens 1 and 2 having thicknesses as shown in Table 13 were prepared. These interference filters thus prepared were then measured for properties by Hitachi's Type 307 Spectrophotometer. The spectral transmittance curves thus determined are shown in Figs. 1-(d) and 2-(d).

5		Remarks	Fig. 1-(d)		Fig. 2-(d)		Fig. 3-(d)	
10		W1/4/W3/4	0.67		0.80		0.62	
20	~ 1	Blocking wavelength band Half value width (nm)	488-522	(34)	492-518	(26)	564-612	(48)
25	TABLE 13		23		50		23	
30 35		Aluminum oxide layer Layer Number thick- of ness (µ) layers	0.106		0.106		0.118	
• 40		Silicon oxide layer Layer Number thick- of ness (µ) layers	23	1	50	Ч	23	Ч
45	-	Silico la Layer thick- ness (µ)	0.057	0.500	0.057	0.500	0.069	0.500
50		Filter specimen	1		2		m	

<sup>55</sup> On the other hand, a filter having a structure shown in Fig. 5 in U.S. Patent No. 2,997,389 was prepared in the vacuum evaporation process to obtain Filter Specimen A.

Filter Specimens A and 1 were then scratched on the surface thereof with the tip of an aluminum diecast of the same material as the insertion holder for band stop filter under substantially the same

pressure. Furthermore, these filter specimens were rubbed on the surface thereof with a dust-covered cloth. As a result, Specimen A had scratches on the surface thereof while Specimen 1 had no scratched on the surface thereof. Thus, it is obvious that Specimen 1 is excellent in scratch resistance as compared to Specimen A.

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When Filter Specimen A was allowed to stand in the atmosphere at an elevated temperature of 100 to 200°C while being irradiated with light, ZnS on the surface thereof was oxidized, lowering the transmittance thereof. This discolored the filter.

When Filter Specimens 1 and 2 were allowed to stand at a temperature of 150°C for 1 hour. there were observed no practical changes in spectral characteristics. There were observed no practical problems in scratch resistance, light resistance and heat resistance.

A Macbeth's color chart, a man, and a natural flower were photographed as objects on a 135-size color negative light-sensitive material (Fuji Color SUPER HR 100) under a 5,500° K light source. The color negative light-sensitive material was subjected to CN-16 standard color development to obtain a color negative film. The images on the color negative film were then printed on Fuji Color Super HR Paper by means of Fuji Color Film Co., Ltd.'s Auto-printer Type 3500 with a band stop filter according to the present invention interposed between the filter source in the autoprinter and the negative filter. For comparison, printing was effected in the same manner as described above except in that no band stop filter was interposed between the light source and the color negative film. These color papers were then subjected to CP-2 standard color development to obtain color prints.

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The color prints obtained with Band Stop Filter Specimen 1 or 2 shows remarkable improvements in fidelity in color reproduction and saturation, particularly of green or yellow system as compared to the color prints obtained without such a filter.

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## EXAMPLE 14

Specimen 3 was prepared in the same manner as in Specimen 1 of Example 13 except in that the film thickness and the number of layers were changed (See Table 13). The spectral transmittance curve of 30 Specimen 3 is shown in Fig. 3-(d).

The same objects as used in Example 13 were photographed on Fuji Photo Film Co., Ltd.'s Fujichrome 100D (135-size). The light-sensitive material was then subjected to CR-56P standard color reversal development to obtain a transparent positive film.

The images on the transparent positive film were then printed on Fuji Color Print by means of Fuji Photo Film Co., Ltd.'s Autoprinter Type 8C 6910 II with Filter Specimen 3 interposed between the light source and the film original and disposed close to the light source. The light-sensitive material was then subjected to RP-303 standard color reversal development to obtain a color print. For comparison, printing was effected in the same manner as described above except in that Filter Specimen 3 was not used. Thus, a comparative color print was obtained.

The color print obtained with Band Stop Filter Specimen 3 according to the present invention showed an excellent color reproducibility, and remarkable improvement in the saturation of a red system as compared to the color print obtained without such a filter.

A color print was obtained in the same manner as described above except in that Filter Specimen 1 was used in combination with Specimen 3. The color print thus prepared showed remarkable improvements in the fidelity in color reproduction of a green system and the saturation of a red system.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

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## Claims

1. A process for the formation of color images which comprises printing on a color printing lightsensitive material comprising a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer provided on a support from a color print original in a subtractive exposure process, and then substantially subsequent color development, characterized in that the effective spectral sensitivity distribution of at least two light-sensitive layers in light-sensitive layers of the color printing light-sensitive material are substantially independent from each other in a wavelength band of 400 to 750 nm and thereby the average color mixing degree in each said light-sensitive layers is 0.13 or less.

A process for the formation of color images as claimed in claim 1, wherein a band stop filter or a
 band stop filter layer is interposed between the light-sensitive layers of the color printing light-sensitive material.

3. A process for the formation of color images as claimed in claim 2, wherein said band stop filter or a band stop filter layer has an absorption band to absorb light in a wavelength range of from 485 nm to 525 nm.

4. A process for the formation of color images as claimed in claim 2, wherein said band stop filter comprises layers prepared by repeatedly applying a plurality of layers comprising a silicon oxide-containing layer and an aluminum oxide-containing layer on a substrate.

5. A purpose for the formation of color images as claimed in claim 1, wherein said color printing lightsensitive material comprises a blue-sensitive layer containing a yellow coupler, a green-sensitive layer rs containing a magenta coupler and a red-sensitive layer containing a cyan coupler provided on a support and satisfies the following conditions A), B) and C)

A) Silver halide emulsion used in the blue-sensitive layer and/or green-sensitive layer is a an emulsion of silver chloride, -silver bromide or silver chlorobromide containing 2 mol% or less of an average silver iodide

B) Silver halide emulsion used in the blue-sensitive layer is not spectrally sensitized or spectrally sensitized using sensitizing dye selected from the group consisting of the compounds represented by the following formula (I) and (II)

C) Silver halide emulsion used in the green-sensitive layer is spectrally sensitized using sensitizing dye selected from the group consisting of the compounds represented by the following formula (III)

 $R_{1}-N = R_{2}$ (CH=CH)<sub>j1</sub>
(CH=CH)<sub>k1</sub>(X<sub>1</sub>)<sub>n1</sub>
(I)

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wherein Z<sub>1</sub> and Z<sub>2</sub> each represent a benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, benzosazole nucleus, naphthoimidazole nucleus, benzoimidazole nucleus, naphthoimidazole nucleus, indolenine nucleus, benzoindolenine nucleus, indole nucleus or guinoline nucleus which may be substituted; R<sub>1</sub> and R<sub>2</sub> each represents an alkyl group, alkenyl group, alkynyl group or aralkyl group; either or both of R<sub>1</sub> and R<sub>2</sub> each has at least one sulfonic acid group, carboxyl group or hydroxyl group; j<sub>1</sub> and k<sub>1</sub> each represents an integer of 0 or 1; n<sub>1</sub> represents an integer of 0 or 1; and X<sub>1</sub><sup>--</sup> represents an acid anion, with the proviso that when n<sub>1</sub> is 0, it indicates that an intramolecular salt is formed.

(II)

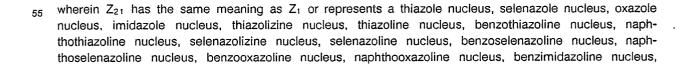
R22

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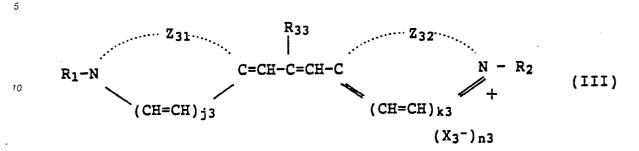
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R<sub>21</sub>-N

(CH=CH)j2



naphothoimidazoline nucleus, pyrroline nucleus, pyrroline nucleus, dihydroprydine nucleus, dihydroquinoline nucleus, benzoimidazoline nucleus or naphthoimidazoline nucleus which may be substituted;  $Q_2$  represents a sulfur atom, oxygen atom, selenium atom or >N-R<sub>23</sub>; R<sub>21</sub>, R<sub>22</sub>, and R<sub>23</sub> each has the same meaning as R<sub>1</sub>; and j<sub>2</sub> has the same meaning as j<sub>1</sub>.



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wherein  $Z_{31}$  has represents benzimidazole nucleus, benzooxazole nucleus, naphthoimidazole nucleus or naphthooxazole nucleus;  $Z_{32}$  represents benzimidazole nucleus, naphthoimidazole nucleus benzooxazole nucleus, naphthooxazole nucleus, benzothiazole nucleus or benzoselenazole nucleus which may be substituted;  $R_{3}$  and  $R_{32}$  each has the same meaning as  $R_1$  and  $R_2$  in the general formula (I);  $R_{33}$  represents a hydrogen atom, lower alkyl group or aralkyl group;  $j_3$  and  $k_3$  has the same meaning as  $j_1$  in the general formula (I);  $n_3$  has the same meaning as  $n_1$  in the general formula (I); and  $X_3^-$  represents an acid anion.

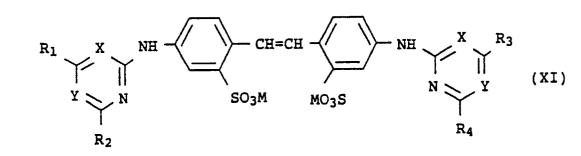
6. A process for the formation of color images as claimed in claim 1, wherein the color mixing degree of a Macbeth chart Y (i = 16) of at least one light-sensitive layer of the color printing light-sensitive material is 0.44 or less.

7. A process for the formation of color images as claimed in claim 1, wherein the average color mixing degree at the printing in each of the light-sensitive layers is 0.12 or less.

8. A process for the formation of color images as claimed in claim 7, wherein the average color mixing degree at the printing in each of the light-sensitive layers is 0.10 or less.

9. A process for the formation of color images which comprises printing on a color printing light-30 sensitive material from a color print original in a substractive exposure process, and subsequently colordeveloping said color printing light-sensitive material, characterized in that said color printing light-sensitive material comprises at least one blue-sensitive layer, at lest one green-sensitive layer and at lest one redsensitive layer provided on a support, said green-sensitive layer has an effective spectral sensitive light amount distribution which is substantially formed by a J-type spectral sensitization, said red-sensitive layer 35 has an effective spectral sensitive light amount distribution which is substantially formed by an M-type or Jtype spectral sensitization, the effective spectral sensitive light amount distribution of said green-sensitive layer and said red-sensitive layer, and/or the effective spectral sensitive light amount distribution of said green-sensitiave layer and said blue-sensitiave layer are substantially independent, and thereby the average color mixing degree at the printing in each of said light-sensitive layers is 0.13 or less and the color 40 development process of said color printing light-sensitive material satisfies the following condition (A) and/or condition (B):

(A) at least one of color development, blix, and rinse and/or stabilization is carried out in the presence of at least one compound represented by the general formula (XI):



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wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each represents a hydroxy group, a halogen atom, a heterocyclic amino group, a heterocyclic thio group, alkoxy group, amino group, alkylamino group, aryloxy group or arylamino group; X and Y each represents = N- or = CH-; and M represents a monovalent cation, with the proviso that X and Y don't represent = CH- at the same time;

(B) the pH value of the bleaching or blix solution is in the range of 3.5 to 6.0 and the replenishing amount of the rinsing solution and/or stabilizing solution is 3 to 50 times the amount of said solution carried over from the pre-bath.

10. A process for the formation of color images as claimed in claim 9, wherein a band stop filter having a spectral absorption band of about 10 to 60 nm in the half value width (W1/2) in a wavelength band excluding the maximum wavelength of the effective spectral sensitive light amount distribution of the each light-sensitive layer  $\pm$  20 nm is used for printing.

11. A process for the formation of color images as claimed in claim 10, wherein a band stop filter having a ratio of 1/4 value width of the spectral transmittance to 3/4 value width of the spectral transmittance (W<sub>1.4</sub>/W<sub>3/4</sub>) of 0.5 or more in the wavelength band for the green-sensitive layer corresponding to the M-type spectral sensitization is used for printing.

12. A process for the formation of color images as claimed in claim 10, wherein said band stop filter comprises layers prepared by repeatedly applying a plurality of layers comprising a silicon oxide-containing layer and an aluminum oxide-containing layer on a substrate.

13. A process for the formation of color images as claimed in claim 9, wherein the average color mixing degree at the printing in each of the light-sensitive layers is 0.12 or less.

14. A process for the formation of color images as claimed Claim 13 wherein the average color mixing degree at the printing in each of the light-sensitive layers is 0.10 or less.

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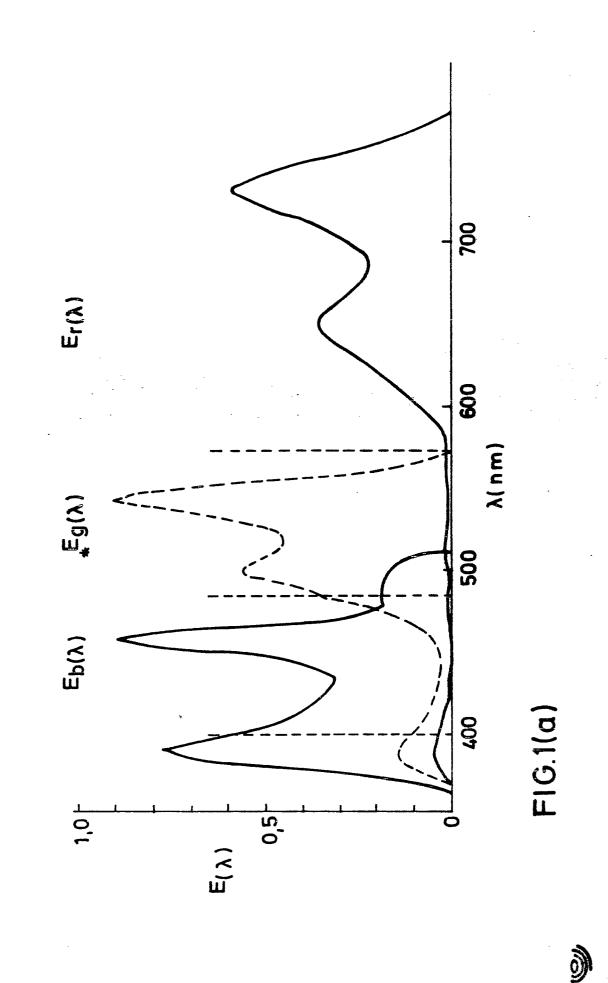
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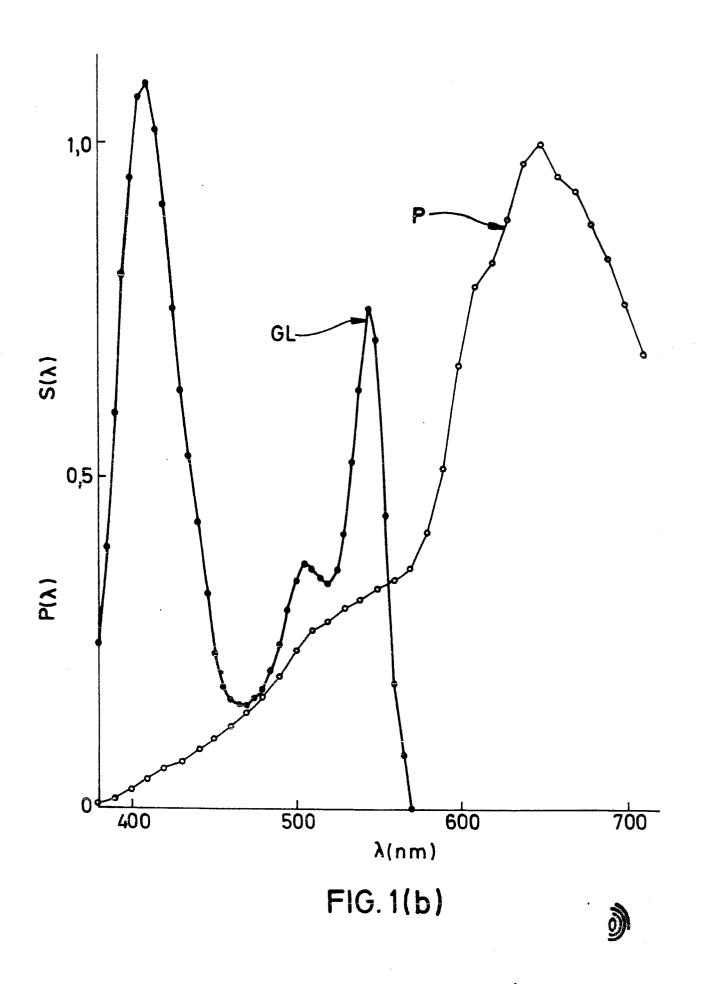
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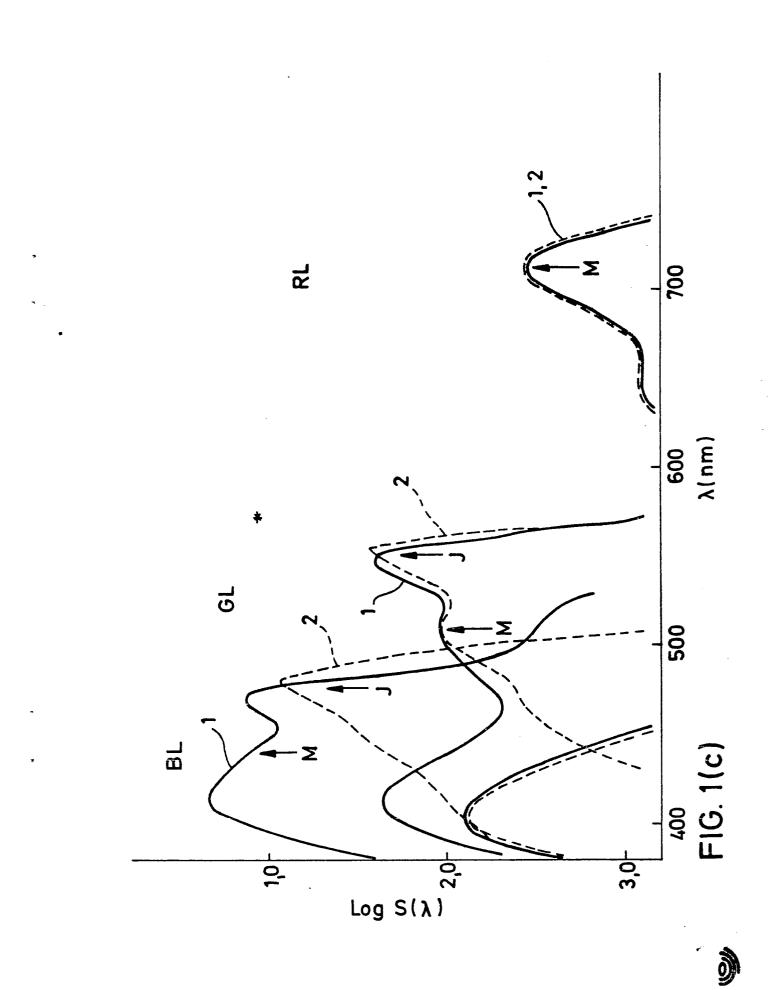
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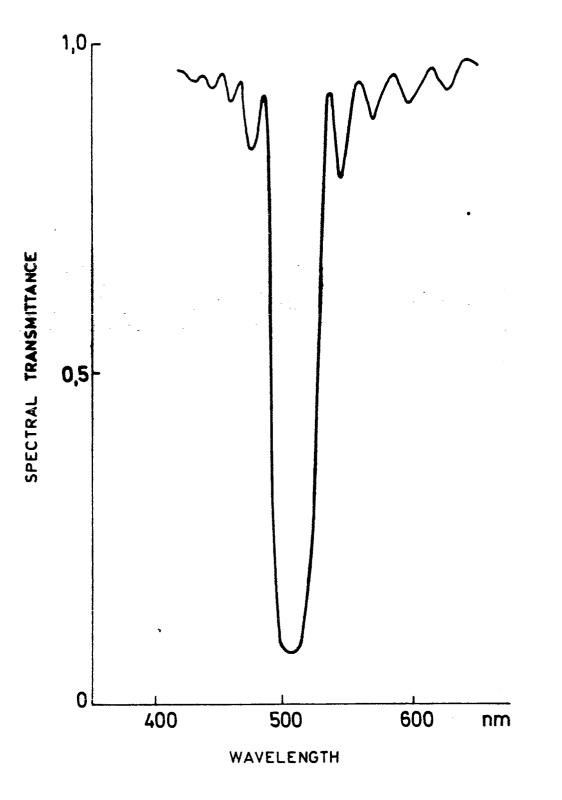
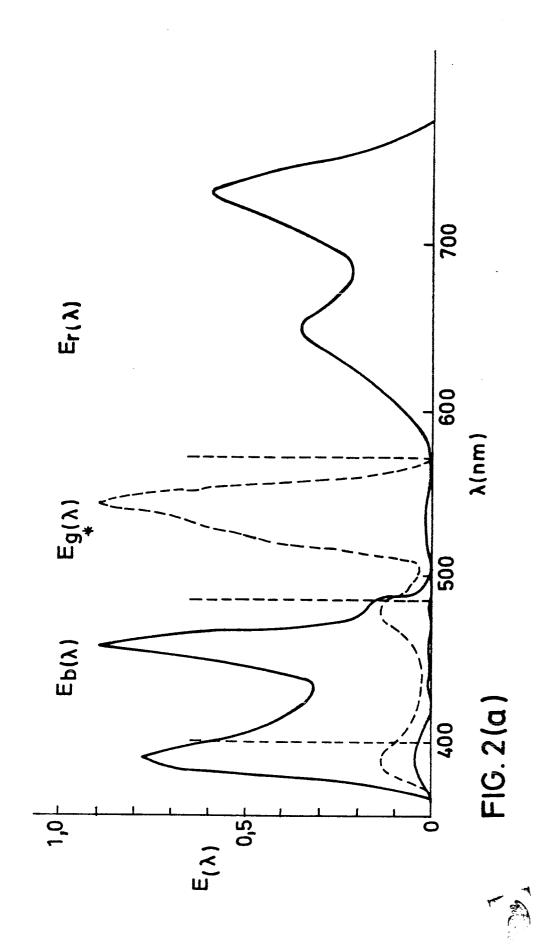
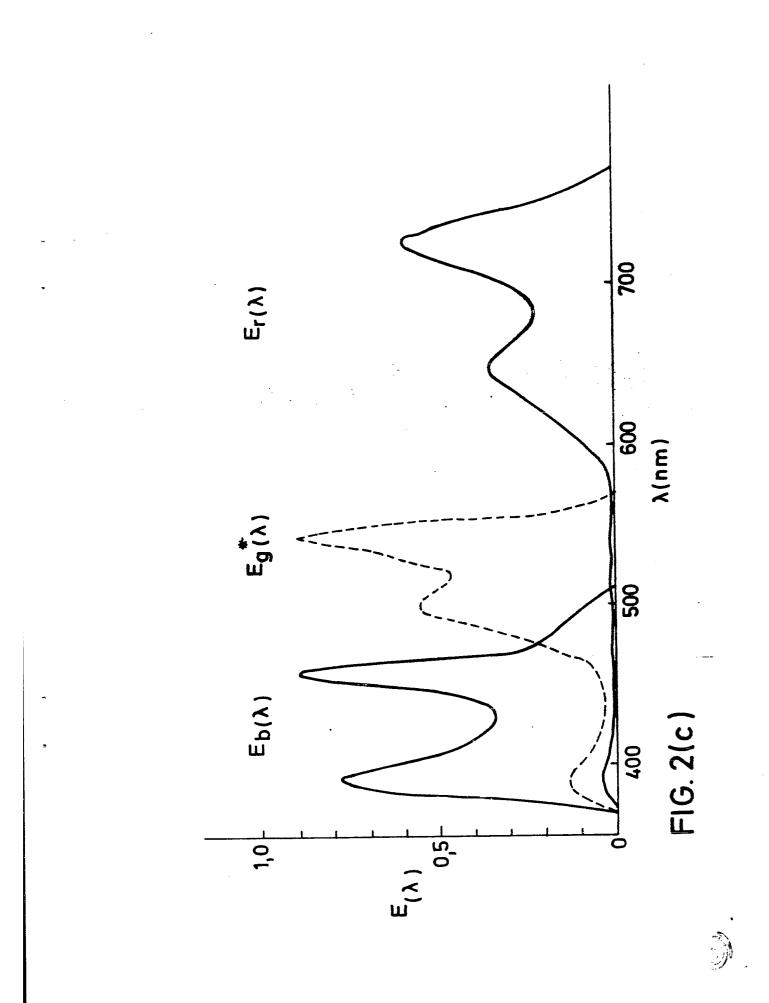


FIG.1(d)



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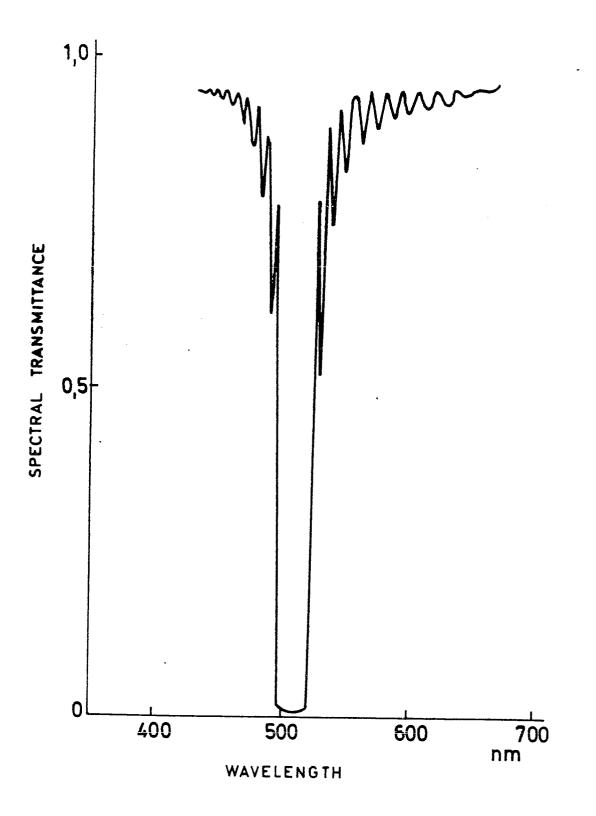
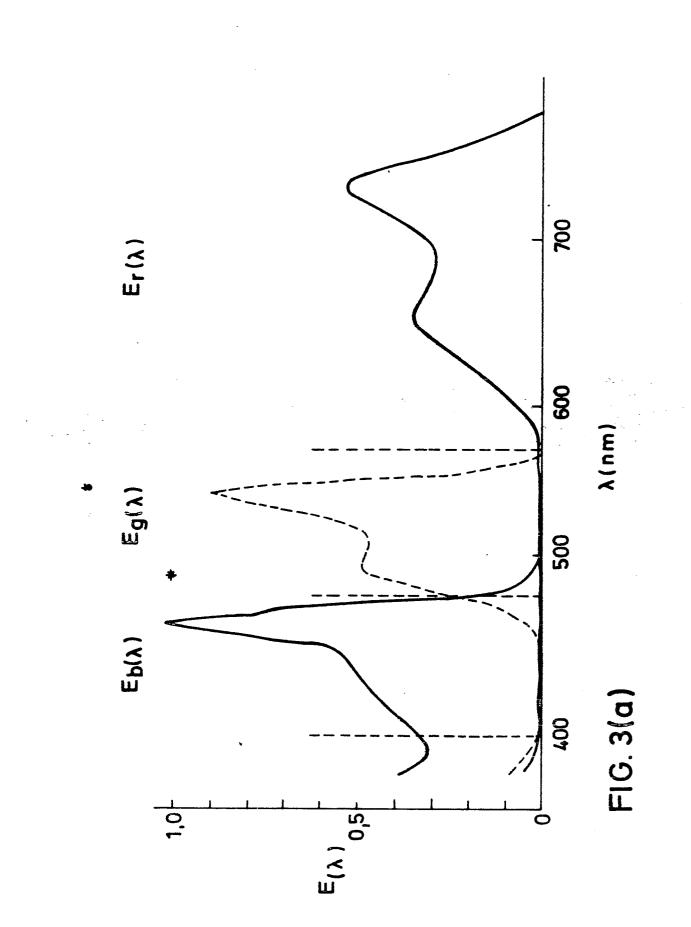


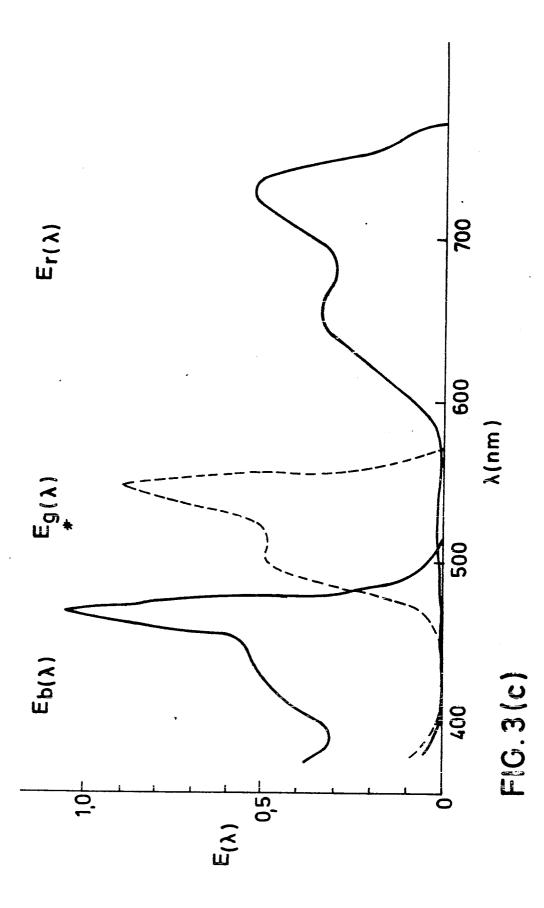
FIG. 2(d)



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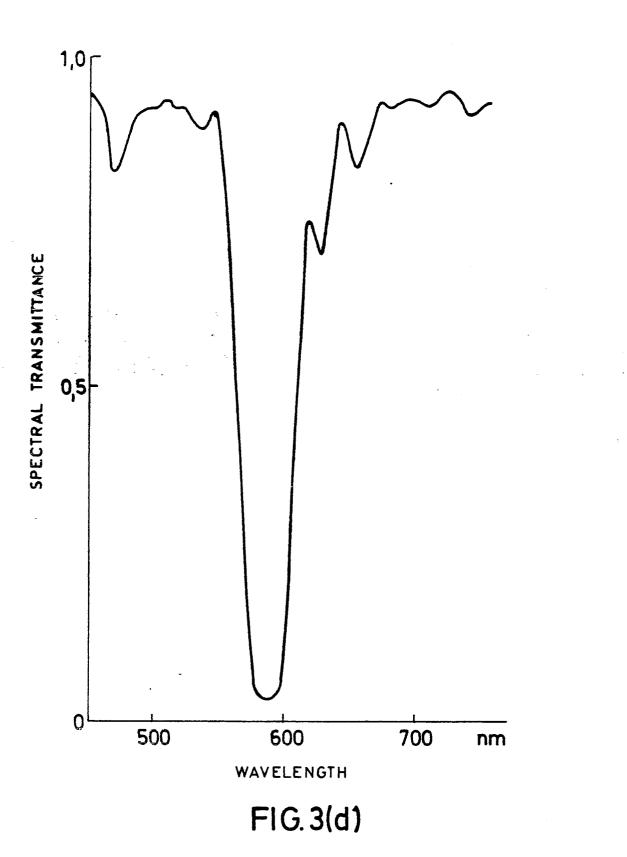
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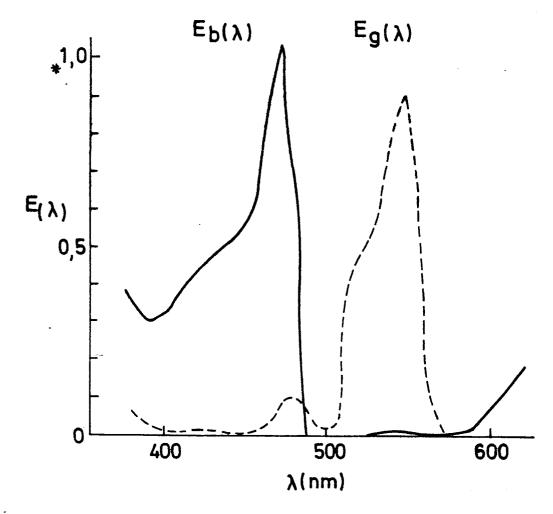
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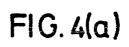


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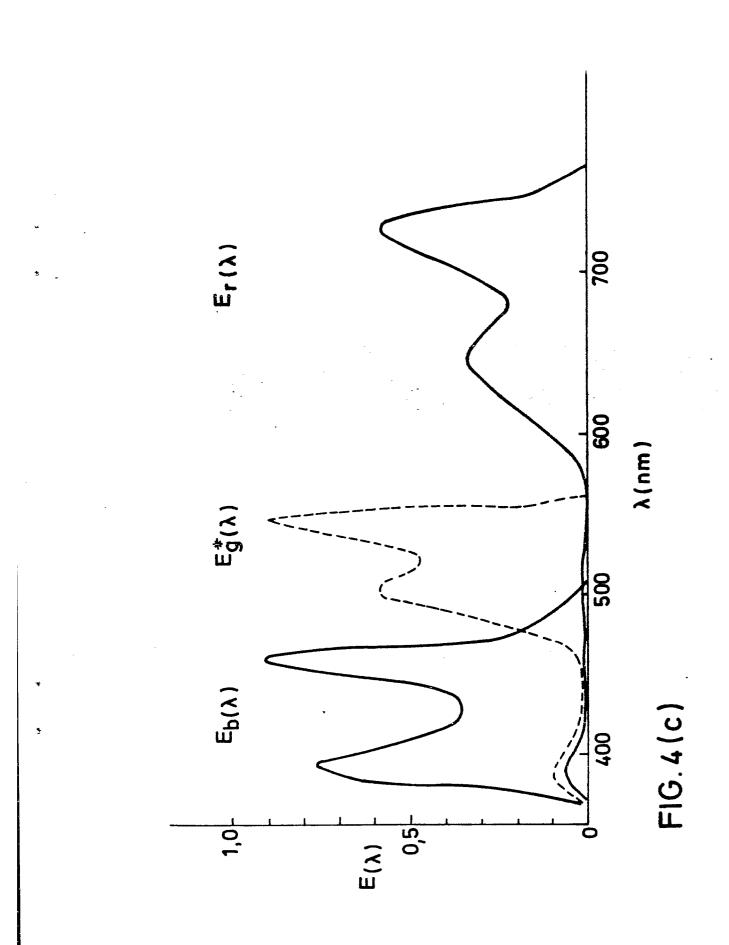
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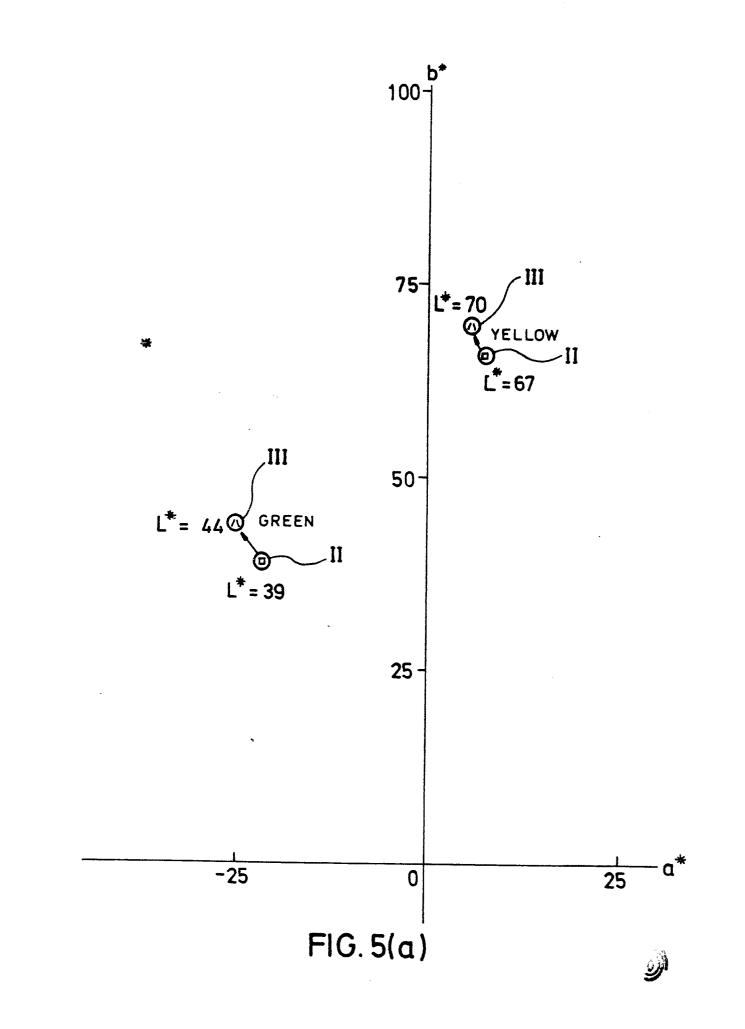




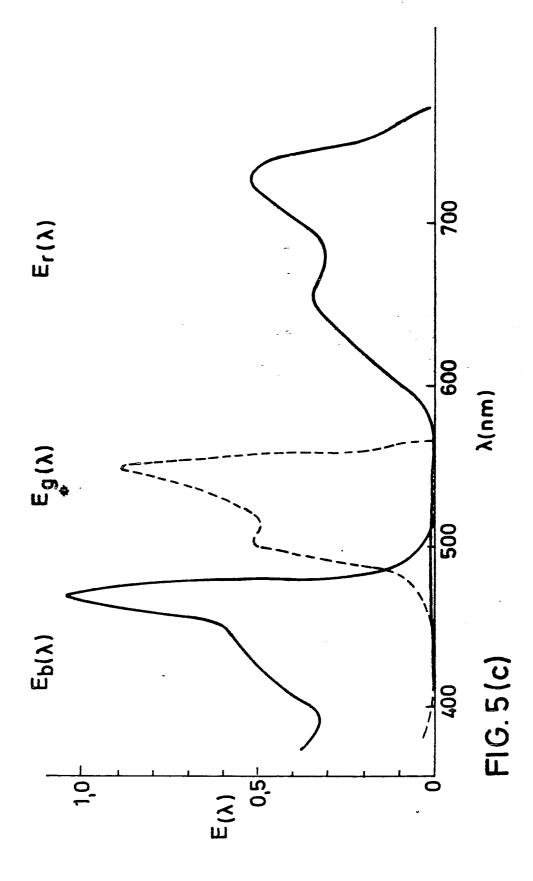
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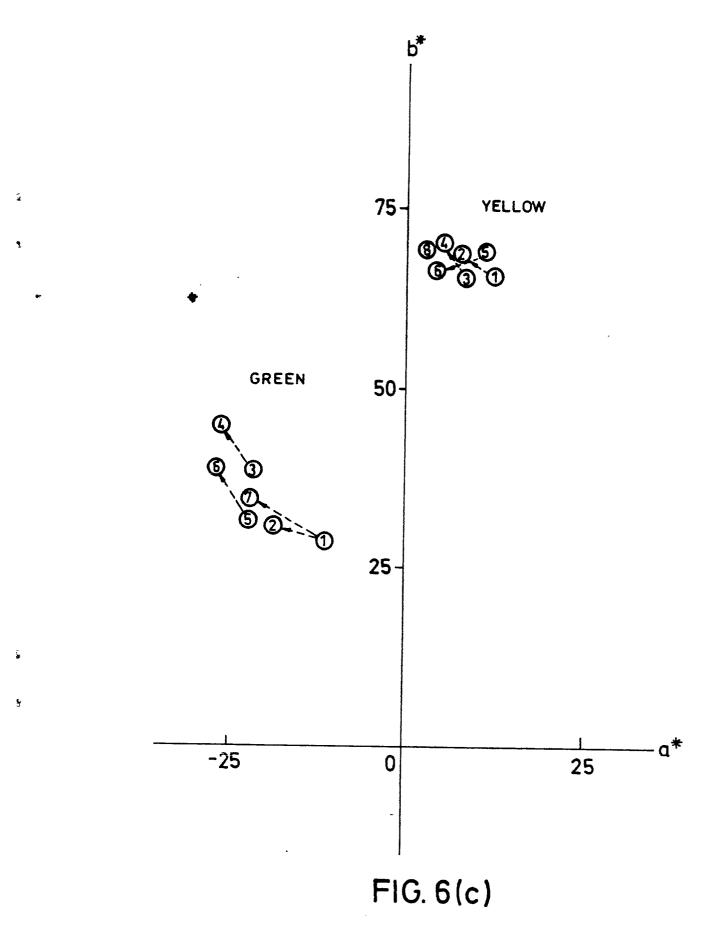
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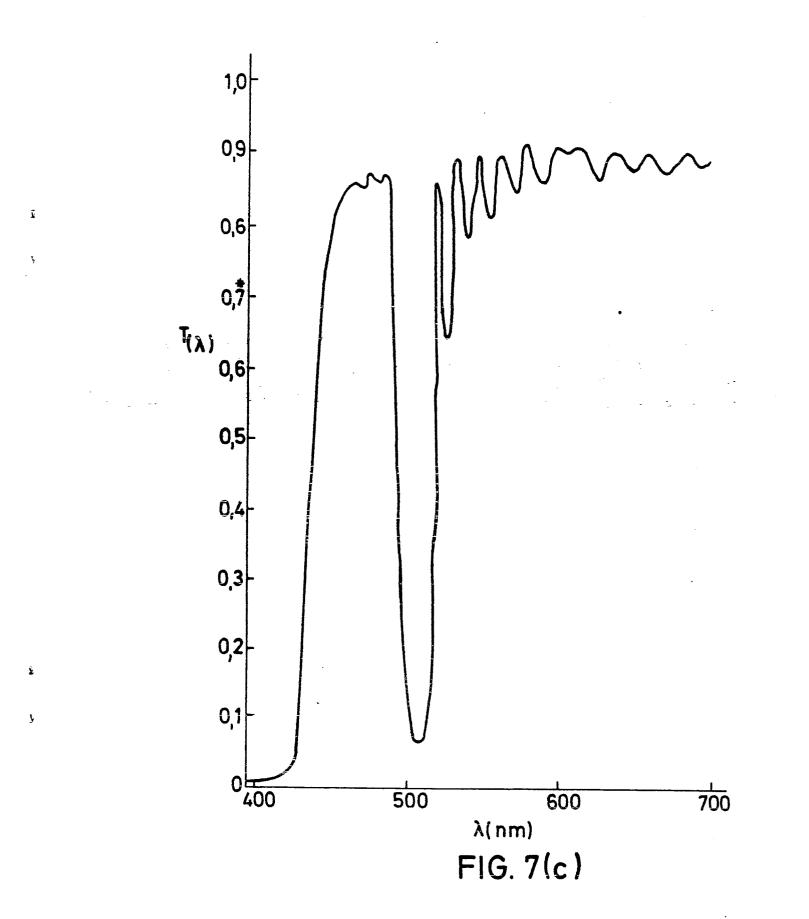
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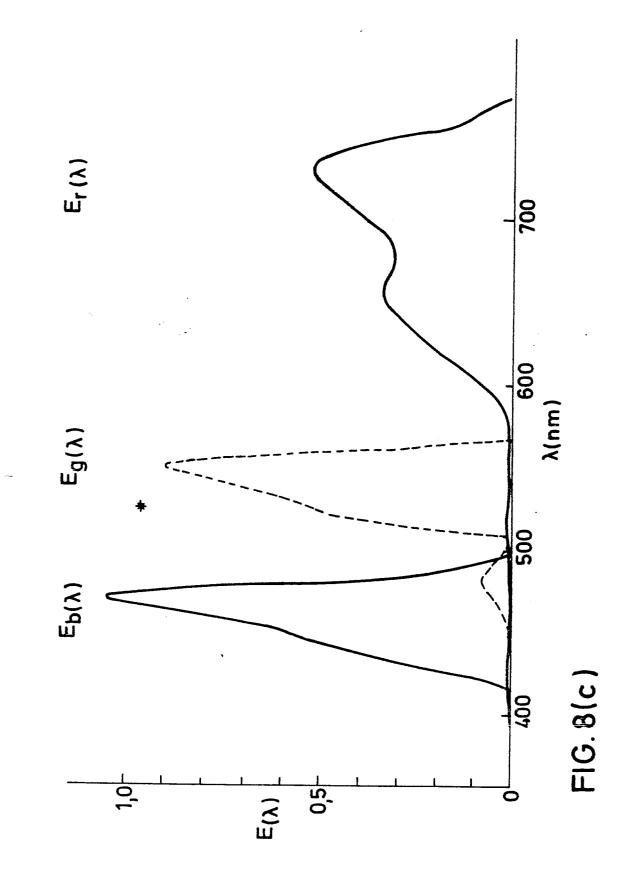


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