(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 351 740 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89112990.0**

(51) Int. Cl.4: **G03C 7/12 , G03C 7/28**

(22) Date of filing: **14.07.89**

(30) Priority: **19.07.88 JP 179625/88**
28.07.88 JP 188632/88

(43) Date of publication of application:
24.01.90 Bulletin 90/04

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **KONICA CORPORATION**
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: **Nishide, Toshikazu c/o Konica Corporation**
1, Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Okauchi, Ken c/o Konica Corporation**
1, Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Mochizuki, Yoshiharu c/o Konica Corporation**
1, Sakura-machi
Hino-shi Tokyo(JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
D-8000 München 80(DE)

(54) Method for preparing color filter and color filter prepared by the method.

(57) There are disclosed a method for preparing color filter which comprises forming at least two color picture elements of at least two colors by effecting at least two pattern exposure to a photosensitive emulsion layer formed on a light-transmissive substrate and then developing the pattern exposed portions, characterized in that the photosensitive emulsion layer contains a dye having a silver dye bleaching effect, at least one color picture element of a color is formed by steps of effecting development of the pattern exposed portions according to the silver dye bleaching method which performs the processing for forming a photosensitive emulsion layer containing a dye, the monochromatic developing processing, the silver dye bleaching processing and the silver bleaching processing in this order, and at least one color picture element of other colors is formed by the steps of effecting development of the pattern exposed portions according to the nonincorporated-coupler type color developing method which employs a developer containing a color forming coupler; and a color filter prepared by the method.

EP 0 351 740 A1

Method for preparing color filter and color filter prepared by the method

BACKGROUND OF THE INVENTION

This invention relates to a method for preparing a color filter, more particularly to a method for preparing a color filter which can control variance which may occur in fine lines of the color filter layer having picture elements even in the case of, for example, preparing a color filter of large area, and also can give a color filter of good image quality by realizing excellent heat resistanoe, flatness and color purity, etc.

A color filter comprising a color filter layer having picture elements of at least two colors on a transparent substrate has been used widely for liquid crystal color display device, color camera tube, color solid image pickup element, etc.

In preparation of a color filter, there has been widely used under the present situation the method in which a color filter is formed on a light-transmissive substrate by employment of the so-called dyeing method.

However, in the liquid color display device comprising the color filter obtained according to the preparation method under the present situation, there is the problem that the image quality is not necessarily satisfactory.

Besides, these problems are more serious in a color filter of large area.

More specifically, in order to obtain a color filter having good image quality without color slippage, color irregularity, image irregularity, etc. according to the dyeing method, the color filter layer having picture elements must be formed on a light-transmissive substrate by effecting uniform exposure to form fine lines of the color filter layer (width about 10 to 20 μm) for respective colors accurately in mosaic shape or stripe shape, but since in the case of a color filter of large area (for example, 300 mm x 150 mm or larger), unevenness of exposure is liable to occur within the plane, it is difficult to realize uniform exposure dosage, whereby fluctuation in width of fine lines of the color filter layer occurs to cause such problems as color slippage, color irregularity, image slippage, etc.

Also, when a color filter of large area is prepared according to the dyeing method under the present situation defects are liable to,occur in the picture element (for example, pinhole, deficiency, so-called horn, etc.), whereby there is also the problem that the production efficiency (so-called yield) of the color filter is low.

As the method for preparing a color filter, there is the nonincorporated-coupler type color developing method by use of color silver salt photographic material.

In the method for preparing a multi-color optical filter utilizing the nonincorporated-coupler type developing method, as described in Japanese Provisional Patent Publication No. 6342/1980, on a photographic material having a light-sensitive silver halide emulsion layer provided on a support, pattern exposure of a first color is effected on the above emulsion layer, then a pattern is formed comprising the dye of the first color and silver is formed according to the nonincorporated-coupler type color developing, subsequently pattern exposure of a second color is effected on the unexposed portion containing silver halide, and then a pattern comprising the dye of the second color and silver is formed according to the nonincorporated-coupler type color developing, and further a similar step to form a pattern comprising the dye of a third color et seq required is repeated, thereby forming a pattern of at least two colors, followed by the desilverization processing after the final color developing processing.

In the above nonincorporated-coupler type color developing method, the present inventors have proposed a method for preparing a color filter according to a combination of a dye having silver dye bleach action and a color forming dye from a coupler by performing silver dye bleach processing, but since the processing steps are entirely different in the silver dye bleach method and external color developing processing method, when the preparation method which performs the external developing processing step is employed after the silver dye bleach processing step, there has been involved the problem that the dye density based on the nonincorporated-coupler type developing processing can not be sufficiently obtained.

The present inventors have further conducted studies to imporve heat resistance and light resistance.

The present invention has been accomplished on the basis of the state of the art as described above.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for preparing a color filter which is free from variance in width of fine lines of the color filter layer even in the case of preparing a color filter of large area, and also which can obtain a color filter capable of realizing good image quality free from color irregularity, color slippage, image irregularity, etc. by realizing excellent heat resistance, flatness and color purity, etc. with good efficiency.

Another object of the present invention is to provide a method for preparing a color filter excellent in production efficiency which can prepare easily and stably a color filter which has excellent color reproducibility based on good spectral characteristics and can be used suitably particularly for color display or color photographing tube, etc., and also can control the reaction and set the reaction conditions easily.

In order to solve the above task, the present inventors have investigated intensively and consequently found that, when picture elements of two or more colors in the color filter layer to be formed on a transparent substrate are formed according to the silver dye bleaching method and the nonincorporated-coupler type color developing method, surprisingly, even when a color filter of large area may be prepared, variance occurring in width of fine lines of the color filter layer can be inhibited, and also a color filter realizing good image quality excellent in heat resistance, flatness and color purity, etc. without color slippage, image irregularity, etc. can be obtained with good efficiency to accomplish the present invention.

A method for preparing a color filter of the present invention comprises forming at least two color picture elements of at least two colors by effecting at least two pattern exposure to a photosensitive emulsion layer formed on a light-transmissive substrate and then developing said pattern exposed portions, characterized in that said photosensitive emulsion layer contains a dye having a silver dye bleaching effect, at least one color picture element of a color is formed by steps of effecting development of said pattern exposed portions according to the silver dye bleaching method which performs the processing for forming a photosensitive emulsion layer containing a dye, the monochromatic developing processing, the silver dye bleaching processing and the silver bleaching processing in this order, and at least one color picture element of other colors is formed by the steps of effecting development of said pattern exposed portions according to the nonincorporated-coupler type color developing method which employs a developer containing a color forming coupler.

A color filter of the present invention comprises in a color filter having been formed at least two color picture elements of at least two colors by effecting at least two pattern exposure to a photosensitive emulsion layer formed on a light-transmissive substrate and then developing said pattern exposed portions, characterized in that said photosensitive emulsion layer contains a dye having a silver dye bleaching effect, at least one color picture element of a color is formed by steps of effecting development of said pattern exposed portions according to the silver dye bleaching method which performs the processing for forming a photosensitive emulsion layer containing a dye, the monochromatic developing processing, the silver dye bleaching processing and the silver bleaching processing in this order, and at least one color picture element of other colors is formed by the steps of effecting development of said pattern exposed portions according to the nonincorporated-coupler type color developing method which employs a developer containing a color forming coupler.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view showing an example of pattern exposure in the preparation method of the present invention;

Fig. 2 is a sectional view showing an example of the color filter obtained according to the preparation method of the present invention;

Fig. 3 is a sectional view show ing similarly another example;

Fig. 4 is a sectional illustration showing an example of the liquid crystal color display by use of a color filter obtained by the preparation method of the present invention;

Fig. 5 is a front view (as viewed from the coated surface) showing an example of the color filter obtained by the preparation method of the present invention; and

Fig. 6 is a sectional view of the same.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As the order of processing in the case of preparing the color filter having picture elements of the three

colors of cyan, magenta and yellow according to the present invention, it can be practiced in the order of, for example, (1) formation of picture elements according to the silver dye bleaching method → formation of picture elements according to the nonincorporated-coupler type color developing method, or alternatively in the order of (2) formation of picture elements according to the nonincorporated-coupler type color forming developing method → formation of picture elements according to the silver dye bleaching method. Further, it can be practiced in the order of (3) formation of picture elements according to the nonincorporated-coupler type color developing method → formation of picture elements according to the silver dye bleaching method → formation of picture elements according to the nonincorporated-coupler type color developing method.

More specifically, in the case of the above order (1), picture elements of either one color of cyan, magenta and yellow are firstly formed according to the silver dye bleaching method, and thereafter picture elements of the remaining two colors are formed according to the nonincorporated-coupler type color developing method.

In the case of the above order (2), picture elements of either two colors of cyan, magenta and yellow are firstly formed according to the nonincorporated-coupler type color developing method, and thereafter picture elements of the remaining one color are formed according to the silver dye bleaching method.

In the case of the above order (3), picture elements of either one color of cyan, magenta and yellow are firstly formed according to the nonincorporated-coupler type color developing method, and thereafter picture elements of either one color of the remaining two colors are formed according to the silver dye bleaching method and finally the remaining one color is formed according to the nonincorporated-coupler type color developing method.

Irrespectively of whether either order may be employed, in the present invention, it is preferred to form picture elements of cyan according to the silver dye bleaching method and picture elements of magenta and yellow according to the nonincorporated-coupler type color developing method.

In the following, concerning the preparation method of the present invention, the formation step of picture elements according to the silver dye bleaching method and the formation step of picture elements according to the nonincorporated-coupler type color developing method are to be described separately.

(Formation of picture elements according to the silver dye bleaching method)

One important point in the method of the present invention is to form at least one color of picture element of the picture elements of two or more colors in the color filter layer to be formed on a light-transmissive substrate by employment of the silver dye bleaching method.

Specifically, a picture element is formed by performing the processing for forming a photosensitive emulsion layer containing a dye (hereinafter sometimes called as photosensitive emulsion layer (A)), the monochromatic developing processing, the dye bleaching processing and the silver bleaching processing are practiced in this order to form picture elements.

Processing for forming photosensitive emulsion layer (A)

In the method of the present invention, the photosensitive emulsion layer (A) is formed on a light-transmissive substrate by coating a photosensitive emulsion (hereinafter sometimes called as photosensitive emulsion (a)) containing a dye.

The above light-transmissive substrate provided to use may be either transparent or translucent, provided that it has light transmissivity. Further, since the color filter may be exposed to high temperature in the vapor deposition step of transparent electrodes etc., the material of the light-transmissive substrate should preferably have good heat resistance.

Examples of the material constituting such light-transmissive substrate may include polymeric compounds such as polyethylene terephthalate, polybutylene terephthalate, polystyrene, polycarbonate, polyether sulfone, polyvinyl alcohol and cellulose acetate; glasses such as soda glass, borosilicate glass, etc.; inorganic substances such as quartz and sapphire, etc.

The above light-transmissive substrate can be used in the form of plate, sheet or film by use of the above material.

The thickness of the above light-transmissive substrate can be set suitably depending on the use and the material, but is generally within the range of 0.5 μm to 10 mm.

Particularly, when a glass is used as the light-transmissive substrate for liquid crystal display device,

the thickness should be preferably within the range of 0.3 to 2 mm.

The surface of the above light-transmissive substrate forming the above photosensitive emulsion layer (A) is not particularly limited, provided that it has surface precision to the same extent as the light-transmissive substrate which has been used in the prior art for a color filter, but for realizing further higher image quality, the surface precision of the light-transmissive substrate should be desirably ± 0.1 μm.

On the surface of the above light-transmissive substrate opposite to the surface where the above photosensitive emulsion layer (A) is formed, a light-transmissive backing layer for antihalation may be also provided. In this case, a dye or a pigment contained in the backing layer should be preferably a non-diffusible dye or pigment. Specifically, a carbon black dispersion can be suitably used. The carbon black dispersion may be also one based on either preparation process of the furnace process and the channel process, and for example, "Diablack" (trade name; manufactured by Mitsubishi Kasei Corporation), etc. can be suitably used.

The above non-diffusible dye or pigment is contained in the backing layer under the state dispersed in hydrophilic colloid, but it must be one which will not be dissolved out into respective processing solutions even after developing processing. The light absorption characteristics of the above non-diffusible dye or pigment are different depending on the spectral absorption characteristics of the silver halide emulsion to be used in the method of the present invention, but for example, when a silver halide emulsion not spectrally sensitized with sensitizing dye is used, it should be preferably one capable of absorbing the light of 500 nm or less. Further, the backing layer may also contain a UV absorber. As the UV-ray absorber, for example, "UVINULMS-40" (trade name; manufactured by BASF Co.), "TINUVIN P" (trade name; manufactured by Ciba Geigy AG) may be employed.

The above non-diffusible dye or pigment and the UV-ray absorber may be used by dissolving in a known high boiling organic solvent and a low boiling organic solvent as represented by methyl acetate, ethyl acetate, propyl acetate, butyl acetate, cyclohexane, tetrahydrofuran, carbon tetrachloride, chloroform, etc., then mixing the solution with an aqueous gelatin solution containing a surfactant, subsequently emulsifying the mixture by means of a dispersing means such as stirrer, homogenizer, colloid mill, flow jet mixer, ultrasonic homogenizer, etc., and then adding the emulsion into the coating composition for hydrophilic colloid backing layer.

The amount of the above non-diffusible dye or pigment used may be preferably 0.1 mg or more, particularly 1 mg or more per 100 cm^2 of the above light-transmissive substrate.

On the surface of the above light-transmissive substrate, the above photosensitive emulsion layer (A) is formed, and it is preferred to provide a subbing layer for reinforcing the adhesive force between the above photosensitive emulsion layer (A) and the above light-transmissive substrate as well as for making the rough surface, if it is, of the above light-transmissive substrate a smooth surface.

As the material for forming the subbing layer, there may be included, for example, gelatin, albumin, casein, cellulose derivatives, starch derivatives, sodium alginate, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid (or polyacrylate) copolymer, polyvinylidene chloride copolymer and polyacrylamide.

The thickness of the above subbing layer may be preferably thin in view of the spectral characteristics of the color filter layer, generally 1 μm or less, preferably within the range of 0.05 to 0.5 μm.

The above photosensitive emulsion (a) provided for use contains at least a silver halide, a water-soluble binder and a dye.

As the above silver halide, for example, silver chloride, silver iodide, silver bromide, silver chloroiodide, silver chlorobromide, silver iodobromide etc. may be included. These may be used either singly or as a combination of two or more kinds. Among them, preferred are silver bromide and silver iodobromide.

For the above silver halide, it is desired to use one having a small average grain size, particularly preferably the so-called Lippmann emulsion having an average grain size of 0.1 μm or less.

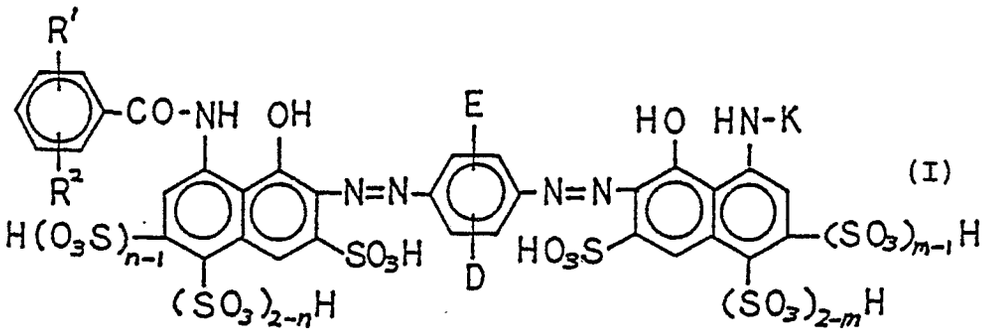
If the average particle size of the above silver halide is large, the sharpness of the color filter obtained may be sometimes lowered.

Examples of the above water-soluble binder may include gelatin, albumin, casein, cellulose derivatives, starch derivatives, sodium alginate, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid (or polyacrylate) copolymer, polyacrylamide, etc. These may be used either singly or as a combination of two or more kinds. Among them, gelatin is preferred.

One of the important points in the present invention is that the above dye contains a dye exhibiting silver dye bleaching action.

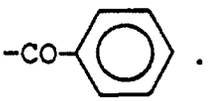
For the above dye, for example, phthalocyanine dyes, azo dyes, etc, can be suitably used. Among azo dyes, particularly preferred are bisazo dyes.

Specifically, there can be exemplified the compounds represented by the following formula (I) with either one of (a) to (k).

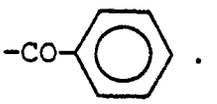


(I)

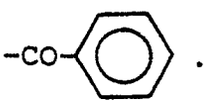
(a) in the above formula (I), compounds wherein R^1 is $-NO_2$, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



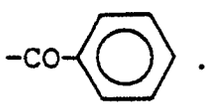
(b) in the above formula (I), compounds wherein R^1 and R^2 are $-NO_2$, D and E are $-OCH_3$ and K is



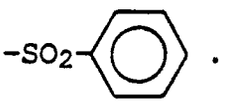
(c) in the above formula (I), compounds wherein R^1 is -Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



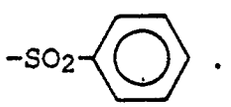
(d) in the above formula (I), compounds wherein R^1 is Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



(e) in the above formula (I), compounds wherein R^1 is -Cl, R^2 and D are hydrogen atoms, E is $-OCH_2CH_2OH$ and K is

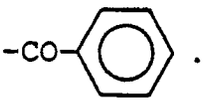


(f) in the above formula (I), compounds wherein R^1 is $-SO_2NH_2$, R^2 and D are hydrogen atoms, E is $-OCH_3$ and K is

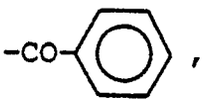


(g) in the above formula (I), compounds wherein R^1 is $-SO_2CH_3$, R^2 is a hydrogen atom, D and E are

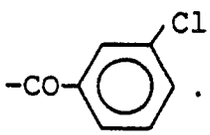
-OCH_3s and K is



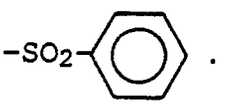
(h) in the above formula (I), compounds wherein R^1 is



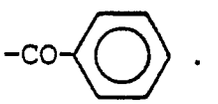
R^2 is a hydrogen atom, D and E are -OCH_3 and K is



(i) in the above formula (I), compounds wherein R^1 is -NO_2, R^2 and D are hydrogen atoms, E is -OCH_2CH_2OH and K is



(j) in the above formula (I), compounds wherein R^1 is -$COCH_3$, R^2 is a hydrogen atom, D and E are -OCH_3s and K is



The above photosensitive emulsion (a) should be preferably one containing the silver halide, water-soluble binder and dye as described above at a weight ratio of (silver halide) : (water-soluble binder) of 1 : 0.5 to 1 : 100, a weight ratio of (silver halide) : (dye) of 1 : 0.1 to 1 : 50 and a weight ratio of (water-soluble binder) : (dye) of 1 : 0.01 to 1:2.

The above photosensitive emulsion layer (A) can be formed by coating the above photosensitive agent on the above light-transmissive substrate by employing the coating method known in the art such as spinner coating, spray coating, etc.

The thickness of the above photosensitive emulsion layer (A) thus formed is generally within the range of 0.3 to 10 μm, preferably 0.5 to 3 μm as dry thickness.

In the method of the present invention, subsequently, after exposure of the above photosensitive emulsion layer (A) was effected, monochromatic developing processing as described in detail below is performed.

For the exposure method, the methods used for conventional pattern exposure (e.g. contact exposure, proxymity exposure, step exposure, etc.) can be employed.

In the method of the present invention, by use of the photosensitive emulsion layer having the photosensitive emulsion layer as described above in detail, after completion of the all processing steps according to the nonincorporated-coupler type color developing method, processing according to the silver dye bleaching method is carried out.

Next, concerning this preparation method of the present invention, the processing step according to the nonincorporated-coupler type color developing method and the processing step according to the silver dye bleaching method are separately described in this order.

(Processing step according to the nonincorporated-coupler type color developing method)

One of the important points in the method of the present invention all the colored portions formed according to the nonincorporated-coupler type color developing method are previously formed on a light-transmissive substrate before applying the silver dye bleaching processing.

Specifically, the above photosensitive emulsion layer can be applied with mask exposure for formation of picture elements, and then subjected to developing processing with a developer containing color forming couplers to form colored portions.

Exposure processing

As the exposure method which can be employed in the method of the present invention, for example, the methods used for conventional pattern exposure such as contact exposure, proximity exposure, step exposure, etc. may be included.

Pattern exposure may be practiced by arranging a photomask 14 on a photosensitive emulsion layer 13 having a photosensitive emulsion layer 12 containing the above dye exhibiting silver dye bleaching action laminated on a light-transmissive substrate 11 as shown in Fig. 1, an irradiating light from above the photomask 14. By this operation, the portion to be exposed 16 of the photosensitive emulsion layer corresponding to the opening 15 provided in the photomask 14 can be selectively exposed. The size of the portion to be exposed 16, namely the size of the opening 15 can be suitably set depending on the use of the color filter. However, if the width of the opening 15 is narrower than the wavelength of the light source used for exposure, no effective exposure can be done and therefore the width of the opening 15 is made wider than the wavelength. Since a silver halide has effective sensitivity to the light within the range of 340 to 420 nm, the width of the opening 15 is generally 340 nm or more, and further in view of the use as the color filter, it should be preferably made 1 μm or more. In the case of a color filter for liquid crystal display, for effective color reproduction by addition color mixing of the respective colored portions of red, blue and green, it is desired that the width of the opening 15 should be set at 1000 μm or less (particularly desirably 500 μm or less).

As other conditions such as exposure time and light source, etc., conventional conditions can be followed.

(Processing step according to the silver dye bleaching method)

The processing steps according to the silver dye bleaching method perform at least monochromatic developing processing, dye bleaching processing and silver bleaching processing in this order.

Next, the processing steps according to the silver dye bleaching method are described and separately about the monochromatic developing processing, the dye bleaching processing and the silver bleaching processing in this order.

Monochromatic developing processing

In the method of the present invention, the above photosensitive emulsion layer subjected to image exposure to the same pattern as the pattern of the desired colored portion of the patterns of the respective colored portions formed according to the above nonincorporated-coupler type color developing method is applied with monochromatic developing processing by use of the monochromatic developer to form a reduced silver image on the above photosensitive emulsion layer.

The above monochromatic developer provided for use contains, for example, a developing agent (hereinafter called as developing agent (D)), a developing aid, a preservative, a so-called developing antifoggant and an alkali buffering agent, and further a solvent for the above developing agent (D) and the developing aid as mentioned above, if necessary.

Examples of the above developing agent may include hydroquinone, chlorohydroquinone, catechol, etc.

Examples of the above developing aid may include pyrazone pyrazone derivatives, Metol, etc.

As the above preservative, sulfites, ascorbic acids, etc. may be included.

Examples of the above developing antifoggant may include bromides, benzotriazole, etc.

Examples of the above alkali buffering agent may include carbonates, hydroxides, phosphates, borates

and metaborates, etc.

Examples of the above so-called antifoggant may include bromides, benzotriazole, etc.

Examples of the solvents for the above developing agent (D) and developing aid may include ethylene glycol, triethanol, diethanol, etc.

To show an example of the contents of the above respective components in the above monochromatic developer, there may be employed 1 to 20 g/liter of the above developing agent (D), 0.05 to 8 g/liter of the above developing aid, 1 to 120 g/liter of the above preservative, 0.001 to 5 g/liter of the above developing antifoggant, 0.1 to 50 g/liter of the above alkali buffering agent, and further when the solvent for the above developing agent and the above developing aid is to be employed, 1 to 20 ml/liter of the above solvent.

The monochromatic developing processing is generally carried out under the conditions of a temperature of 20 to 60 °C, for 10 to 200 seconds, by dipping the photosensitive emulsion layer (A) subjected to the above image-exposure in a developing bath housing the above monochromatic developer.

By the monochromatic developing processing, a reduced silver image (silver negative image) is formed in the photosensitive emulsion layer (A) subjected to the above image exposure.

In the present invention, after the monochromatic developing processing, water washing processing is generally practiced before carrying out the dye bleaching processing described in detail below.

Dye bleaching processing

In the dye bleaching processing, bleaching of the dye of the above dye contained in the above photosensitive emulsion layer is effected by use of a dye bleaching solution.

More specifically, the dye bleaching processing is a processing in which a positive-image of the above dye is formed by bleaching the dye at the portion containing more image silver among the dyes in the above dye contained in the photosensitive emulsion layer subjected to the above image exposure.

The above dye bleaching solution provided for use may contain, for example, a bleaching agent, a compound forming a silver salt or a silver complex and a dye bleaching promoting catalyst.

As the above bleaching agent, for example, mineral acids such as hydrochloric acid, sulfuric acid, nitric acid, etc.; organic acids such as sulfamic acid, succinic acid, acetic acid, etc. may be included.

As the compound forming the above silver salts or silver complex, there may be included, for example, potassium bromide, potassium iodide, urea, thiourea, semicarbazide, thiosemicarbazide, etc.

Examples of the above dye bleaching promoting catalyst may include pyrazine, naphthazine, quinoline, quinoxalines, phenazines, anthraquinones, naphthoquinones, indophenazines, N-substituted isoaroxazines, furoquinoxalines, thienoquinoxalines, diphenyl derivatives, triphenylmethane derivatives, lumazins, alloxazines, cinnolines, orthophenylenediamine derivatives, etc. (see U.S. Patents No. 2,270,118, No. 2,410,025, No. 2,541,884, No. 2,627,461 and No. 2,669,517, U.K. Patents No. 657,374 and No. 711,247, Japanese Patent Publication No. 22195/1970).

To show an example of the contents of the above various components in the dye bleaching solution, there may be employed 1 to 20 g/liter of the above bleaching agent, 0.1 to 20 g/liter of the compound forming the above silver salt or silver complex, and 0.001 to 10 g/liter of the above dye bleaching promoting catalyst.

In the present invention, dye bleaching processing is practiced generally by dipping in a dye bleaching solution under the conditions of a temperature of 20 to 60 °C for 10 to 200 seconds.

By this dye bleaching processing, more bleaching is effected as the amount of image silver subjected to the above image exposure is more in the photosensitive emulsion layer to form a positive image of the dye and, the black silver which was not utilized for bleaching of the dye may sometimes remain as such.

In the present invention, after the dye bleaching processing, water washing processing can be generally practiced before carrying out the silver bleaching processing which is described in detail below.

Silver bleaching processing

Silver bleaching processing is a processing in which all the black silver remaining in the photosensitive emulsion layer subjected to image exposure and the above dye bleaching processing is rehalogenated to be converted to silver chloride.

For this silver bleaching processing, a silver bleaching solution is used.

The above silver bleaching solution may be one which has been known in the art, for example, a bleaching solution containing ferric chelate containing ethylenediamine-tetraacetate can be preferably used.

In the present invention, the silver bleaching processing may be generally conducted under the condition of a temperature of 18 to 60 °C for 5 to 500 seconds.

When the picture element finally formed in the present invention is according to the dye bleaching method, after the silver bleaching processing, the respective processings of water washing → fixing → water washing → stabilizing → drying can be performed in conventional manners to form a color filter layer having a picture element of either one color of cyan, magenta and yellow.

On the other hand, when picture elements of another color are to be formed according to the nonincorporated-coupler type color developing method after formation of picture elements according to the silver dye bleaching method, after the above silver bleaching processing, the nonincor porated-coupler type color developing method as described below can be practiced after washing and drying.

(Formation of picture element according to the nonincorporated-coupler type color developing method)

One of the important points in the method of the present invention is to form the remaining picture elements of other colors excluding the picture elements of at least one color formed according to the above silver dye bleaching method of the picture elements of two or more colors to be formed on a light-transmissive substrate by employment of the nonincorporated-coupler type color developing method.

Specifically, after the photosensitive emulsion layer (A) formed by coating on the light-transmissive substrate is processed by the silver dye bleaching method to form picture elements mask exposure for picture element formation is applied and developing processing with a developer containing a color forming coupler can be performed to form picture elements. Alternatively, before forming picture elements according to the silver dye bleaching method, picture elements according to the nonincorporated-coupler type color developing method can be also formed on the photosensitive emulsion layer (A) by employment of the above method.

In this nonincorporated-coupler type color developing method, for the exposure method, there can be employed the method used for conventional pattern exposure similarly as in exposure in the case of the above silver dye bleaching method (e.g. contact exposure, proximity exposure, step exposure, etc.).

Developing processing

The nonincorporated-coupler type color developing method is a method in which developing is performed by use of a developer, thereby having the dye dyed or precipitated into the above photosensitive emulsion layer (A).

The above developer provided for use contains at least a color forming coupler and a developing agent (hereinafter called as developing agent (d)).

As the above developing agent (d), the compounds described in "The Theory of Photographic Process, 3rd Edition, written by C.E.K. Mees and J.T. James, pp. 293 - 298" can be included, and specific examples thereof may include

(1) 4-amino-3-methyl-N-(2-hydroxyethyl)aniline sulfate
(2) N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine/p-toluenesulfonate
(3) 4-amino-3-methyl-N-ethyl-N-(2-methylsulfonamideethyl)aniline sulfate•hydrate
(4) N,N-diethyl-p-phenylenediaminesulfate and
(5) N,N-diethyl-3-methyl-p-phenylenediamine hydrochloride.

In the above developer, from among the developing agents including the developing agents shown as examples, one kind of developing agent is selected and used. Selection of the developing agent is generally done in view of the kind and combination of the color forming coupler, etc.

The above developing agent (d) in the developer is generally used so that it may be contained in an amount within the range of 0.1 to 10 g in 1 liter of the developer.

Particularly, it is preferred to use the developing agent (d) in an amount within the range of 0.5 to 7 g in one liter of the developer, further it is particularly preferred to use the developing agent (d) in an amount within the range of 1 to 5 g.

By setting the formulation amount of the developing agent (d) within such a range, the developing time at an ordinary temperature can be made within an adequate range (for example, within 1 to 10 minutes) regardless of the kind of the color forming coupler used, whereby workability becomes extremely good. Further, by setting the amount within this range, color formability tends to become particularly good.

In the above color developer, two or more kinds of color forming couplers exhibiting different color

formations are contained.

More specifically, color forming couplers can be classified into magenta color forming coupler, cyan color forming coupler and yellow color forming coupler depending on the wavelength for color formation. And, in the nonincorporated-coupler type color developing method in the present invention, two kinds of these or color forming couplers exhibiting two kinds of different color formations are used in combination.

Since the combination of these color forming couplers exhibits the color appearing in picture elements through detractive color mixing, by combining a magenta color forming coupler with a cyan color forming coupler, a blue color forming developer is formed, by combining a yellow color forming coupler with a cyan color forming coupler, a green color forming developer is formed, and by combining a magenta color forming coupler with a yellow color forming coupler, a red color forming developer is formed. And, by combining coupler color forming agents exhibiting three kinds of different color formations of magenta color forming coupler, cyan color forming coupler and yellow color forming coupler, a black color forming developer is formed.

The above color forming coupler is different from the incorprated coupler (ballast type coupler) used in conventional color photographic process, and is a non-incorporated-coupler type coupler which is used by being added into a developer and under the state at least partially dissolved in the developer, and known nonincorporated-coupler type couplers can be used.

Of the above color forming couplers, examples of yellow color forming couplers can include ring-opened ketomethylene compounds (e.g., acylacetanilide such as 2-(p-carboxyphenoxy)-2-pyvaloyl-2′,4′-dichloroacetanilide, etc.), and further in the present invention, those disclosed in U.S. Patents No. 3,510,306 and No. 3,619,189, Japanese Patent Publications No. 33775/1965 and No. 3664/1969 can be used.

Examples of magenta color forming couplers can include active methylene compounds (e.g. hydrazones and cyanoacetanilides such as 1-(2,4,6-trichlorophenyl)-3-(p-nitroanilino)-2-pyrazolino-5-one, etc.), and further in the present invention, those disclosed in West German OLS 2,016, 587, U.S. Patents No. 3,152,896 and No. 3,615,502, and Japanese Patent Publication No. 133111/1969 can be used.

Further, examples of cyan color forming couplers can include phenol compounds (e.g., 2-acetamido-4,6-dichloro-5-methyl-phenol) or naphthol compounds (e.g., N-(O-acetamidephenoethyl)-2-hydroxy-2-naphthoamide), and also in the present invention, those disclosed in U.S. Patents No. 3,002,836 and No. 3,542,552 and U.K. Patent No. 1,062,190 can be used.

Also, concerning the color forming couplers which can be used in the nonincorporated-coupler type developing method, in addition to those mentioned above, those described in "The Theory of Photographic Process 3rd Edi tion, Chapter 17, written by C.E.K. Mees and J.T. James, pp. 382 - 395" can be also used.

In the above developer, the total content of the color forming couplers in one liter of the developer should be preferably set within the range of 0.5 to 20 g. If it is less than 0.5 g, no sufficient color formation may be sometimes effected, while on the other hand, if it is used in an amount of more than 20 g, the so-called fog may be sometimes generated. Particularly, in this special nonincorporated-coupler type developing method, by making the total content of the color forming couplers in one liter of the developer within the range of 1 to 10 g, a color filter layer with little color contamination and good spectral characteristics can be obtained.

The formation ratio of the color forming couplers exhibiting different color formations in the developer can be suitably set in view of the color forming characteristics of the color forming couplers used. For example, when a cyan color forming coupler is used in combination with a magenta color forming coupler, the weight ratio of the both is made generally within the range of 1 : 9 to 7 : 3, preferably 1 : 9 to 4 : 6. On the other hand, when a cyan color forming coupler is combined with a yellow color forming coupler, the weight ratio of the both is made generally with the range of 1 : 9 to 7 : 3, preferably 1 : 9 to 4 : 6. Further, when a magenta color forming coupler is combined with a yellow color forming coupler, the weight ratio of the both is made generally within the range of 9 : 1 to 2 : 8, preferably 8 : 2 to 6 : 4. And, when the three of a cyan color forming coupler, a magenta color forming coupler and a yellow color forming coupler are combined, it is preferred to formulate the three in substantially equal amounts.

As for the formulation weight ratio of the total amounts of the above color forming couplers to the above develop ing agent (d) in the developer which can be suitably used in the nonincorporated-coupler type color forming developing method in the method of the present invention can be set suitably in view of the kinds and contents of the above color forming couplers and the developing agent (d), but usually the formulation weight ratio of the color forming couplers and the above developing agent (d) is made within the range of 1 : 9 to 9 : 1.

Further, the above developer may also contain additives which are contained in conventional nonincorporated-coupler type developers such as preservatives (e.g., sodium sulfite, diethylhydroxylamine), accelerators (e.g., alkali agents such as sodium hydroxide), controlling agents (e.g., potassium bromide,

potassium iodide), aids (e.g., water quality controllers such as polyethylene glycol, etc., tone controllers such as citrazinic acid, imidazole derivatives, etc.) etc

The above developer can be prepared by dissolving the above components in water.

The above developer may be controlled to a pH value of 9.0 to 13.0 at ordinary use temperature (e.g., 10 to 40 °C) with the use of sodium hydroxide, etc. before it is used.

In the method of the present invention, formation of the color filter layers of the picture elements with other colors than one color formed by employment of the above silver dye bleaching method can be practiced by use of the above developer as described below.

First, the above photosensitive emulsion layer (b) is subjected to pattern exposure in conventional manner (the first exposure).

After the first pattern exposure is effected, the first developing of the exposed portion is carried out by use of the developer containing the above color forming couplers. For example, by carrying out development by use of a developer containing a cyan color forming coupler and a magenta color forming coupler as the color forming couplers (blue developer), the exposed portion is developed to blue color. On the other hand, by use of a developer containing a cyan color forming coupler and a yellow color forming coupler (green developer), the exposed portion is developed to green color. Further, by use of a developer containing a magenta color forming coupler and a yellow color forming coupler (red developer), the exposed portion is developed to red color. The first exposed portion may be developed with either developer of the above blue developer, green developer and red developer.

Also, by use of a developer containing a cyan color forming coupler (cyan developer), a developer containing a magenta color forming coupler (magenta developer) and a developer containing a yellow color forming coupler (yellow developer), the exposed portion is developed to cyan color, magenta color and yellow color, respectively.

After the first exposed portion is thus developed, the reaction accompanied with development is generally stopped by dipping the above photosensitive emulsion layer (b) in a solution containing acetic acid and sodium sulfate, and subsequently the photosensitive emulsion layer (b) is washed with water and dried, thereby forming the first colored portion having picture elements of either red color, blue color and green color.

Next, by use of a photomask, the unexposed portion adjacent to the above first exposed portion is subjected to pattern exposure in the same manner as in the first exposure, and then developed by use of one kind of the developers other than that used in the first step. Further, via the steps of dipping into a stopping solution, water washing and drying, etc., if desired, the second exposed portion can be formed.

After the first and the second colored portions are thus formed, the colored portions are generally fixed in the step of removing the silver component in the photosensitive emulsion layer (b) (bleaching step).

Thus, on the above light-transmissive substrate, there can be prepared a color filter layer having picture elements of remaining colors excluding picture elements of at least one color formed by applying the above silver dye bleaching method of red color (R), blue color (B) and green color (G).

In this method of the invention, for example, after light-transmissive colored portion 32 comprising red portion (R), blue portion (B) and green portion (G) are formed with gaps being provided therebetween on a light-transmissive substrate 31 as shown in Fig. 3, the gaps can be applied with pattern exposure and then subjected to developing processing with the use of a developer containing a cyan color forming coupler, a magenta color forming coupler and a yellow color forming coupler, whereby light-transmissive sections (black stripe) 33 can be also formed at the gaps between the colored portions 32 of red portion (R), blue portion (B) and green portion (G). Also, in that case, the silver dye bleaching process is conducted after completion of all the nonincorporated-coupler type developing process.

Also, in this method of the invention, depending on the use of the color filter, the color filter layer can be subjected to etching treatment to remove unnecessary portions of the color filter layer.

Further, the formation mode of picture elements may be either one of mosaic shape and stripe shape.

The color filter thus obtained can be used suitably as the filter for liquid crystal color display as shown in Fig. 4. More specifically, as shown in Fig. 4, by arranging the color filter 43 so that the color filter 43 and the liquid crystal 47 controlled by the electrodes 48a and 48b may be sandwiched between the polarizing plates 46a and 46b, it can be used as the filter for liquid color display.

Further, otherwise it can be also suitably used in place of the color filter for photographing tube which has been used in the prior art.

EXAMPLES

The present invention is described in detail by referring to Examples.

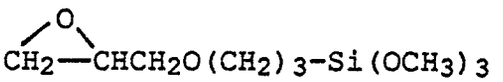
Example 1

Preparation of silver halide photographic material

A silver iodobromide emulsion containing 3 mole % of silver iodide was prepared by adding an aqueous silver nitrate solution and an aqueous solution containing potassium bromide and potassium iodide at the same time into an aqueous 10 % gelatin solution. The addition conditions were regulated so that Lippmann's emulsion having an average grain size of 0.05 μm was obtained. The emulsion was chemically aged with sodium thiosulfate under the condition of a temperature of 60 °C for 100 minutes. The amount of silver per one liter of the emulsion was made 31.8 g.

Subsequently, to one liter of the above emulsion were added 159 cc of an aqueous 2 % solution of a cyan dye (Exemplary compound (g)), 20 cc of an aqueous 2 % Alkanol XC solution (produced by Du Pont Co.), and further 40 mg and 5 mg of the compounds H-1 and H-2 as the film hardener per 1 g of gelatin to prepare an emulsion coating solution.

Compound H-1



Compound H-2

$[(CH_2=CHSO_2CH_2)_3CCH_2SO_2CH_2CH_2]_2N\text{-}CH_2CH_2SO_3K$

The above emulsion coating solution was applied onto a transparent borosilicate glass substrate (30 cm x 30 cm) with a thickness of 1.1 mm to a dry film thickness of 2 μm to prepare a light-sensitive silver halide photographic material. The amount of silver attached was 1.5 g/m^2, and the cyan dye (Exemplary compound (g)) attached 0.15 g/m^2.

Preparation of color filter

The method for preparing a color filter having a mosaic pattern of the three colors of B (blue), G (green) and R (red) as shown in Fig. 5 is to be described below. The size of each picture element is 150 μm x 150 μm.

With a chromium mask for color filter having a square opening with one side of 150 μm being superposed on the above photographic material, the first exposure was effected by use of a tungsten lamp. Exposure was effected at the position corresponding to the part B in Fig 5.

The exposed photographic material was dipped in the following magenta color developing solution shown below at 23 °C for 3 minutes.

Magenta color developing solution composition

A	Magenta coupler 7-Chloro-3,6-dimethyl-1H-pyrazolo-[5,1-c]-1,2,4-triazole	1.24 g
	Methanol	25 ml
B	Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate	0.93 g
	Anhydrous sodium sulfite	2.0 g
	Hydroxylamine sulfate	2.0 g
	Sodium carbonate monohydrate	50.0 g
	Potassium bromide	2.5 g
	Pure water	800 ml

After A was mixed with B, water was added to make up the total amount to one liter, and the mixture was adjusted to pH 11.5 (23 °C) with sodium hydroxide.

Next, the photographic material was dipped in a stopping solution (containing 32 ml of 28 % acetic acid and 45 g of sodium sulfate in one liter) for 30 seconds and washed with water for 5 minutes, and then bleached with a silver bleaching solution having the following composition (23 °C, 2 minutes), followed by washing with water for 2 minutes and drying, to form a magenta dye on the substrate.

Silver bleaching solution composition	
Ammonium bromide	160.0 g
Aqueous ammonia (28 %)	25.0 ml
Iron sodium ethylenediaminetetraacetate	130.0 g
Glacial acetic acid	14.0 ml
Water is added to make up the total amount to one liter.	

Next, on the photographic material after the above processing, another chromium mask for color filter was arranged so that the exposed portion became the part G in Fig. 5 and the second exposure was effected.

The photographic material subjected to the second exposure was dipped in a yellow color developing solution having the following composition at 23 °C for 3 minutes, then dipped in the above stopping solution for 30 seconds and then washed with water for 5 minutes, followed by bleaching, water washing and drying similarly as the first time to form a yellow dye on the substrate.

Yellow color developing solution composition

A	Yellow coupler α-(2-Carboxyphenoxy)-α-pivaloyl-2,4-dichloroacetanilide	1.02 g
	Methanol	25 ml
B	Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-methoxyethyl)aniline·p-toluenesulfonate	1.05 g
	Anhydrous sodium sulfite	2.0 g
	Hydroxylamine sulfate	2.0 g
	Sodium carbonate·monohydrate	50.0 g
	Potassium bromide	2.5 g
	Pure water	800 ml

After A was mixed with B, water was added to make up the total amount to one liter, and the mixture was adjusted to pH 11.5 (23 °C) with sodium hydroxide.

Next, on the photographic material after the above processing, another chromium mask for color filter was arranged so that the exposed portion became the part R in Fig. 5, and the third exposure was effected.

The photographic material subjected to the third exposure was dipped in a red color developing solution having the following composition at 23 °C for 3 minutes, followed by stopping, bleaching, water washing and drying similarly as in the second time to form magenta and yellow dyes on the substrate.

Red color developing solution composition

A	Magenta coupler 7-Chloro-3,6-dimethyl-1H-pyrazolo-[5,1-c]-1,2,4-triazole	1.24 g
	Yellow coupler α-(2-Carboxyphenoxy)-α-pivaloyl-2,4-dichloroacetanilide	1.02 g
	Methanol	25 ml
B	Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate	0.93 g
	Anhydrous sodium·sulfite	2.0 g
	Hydroxylamine sulfate	2.0 g
	Sodium carbonate monohydrate	50.0 g
	Potassium bromide	2.5 g
	Pure water	800 ml

After A was mixed with B, water was added to make up the total amount to one liter, and the mixture was adjusted to pH 11.5 (23 °C) with sodium hydroxide.

Next, on the photographic material after the above processing, a chromium mask for color filter was arranged so that the exposed portion became the part R in Fig. 5, and the fourth exposure was effected.

The photographic material subjected to the fourth exposure was processed as follows under the condition of a temperature of 33 °C.

Monochromatic developing	1 minute
Water washing	1 minute
Dye bleaching	1 minute
Water washing	1 minute
Silver bleaching	1 minute
Water washing	1 minute
Fixing	1 minute
Water washing	4 minutes
Drying	

Here, the baths used for the respective processings have the following compositions.

<Monochromatic developer composition>	
Sodium sulfite	20 g
Hydroquinone	10 g
Potassium hydroxide (48 % aqueous solution)	5 cc
Diethylene glycol	20 cc
Dimedone	0.7 g
Sodium carbonate	20 g
Potassium bromide	9 g
Thiadiazole	0.05 g
Water added to	one liter

<Dye bleaching solution composition>	
96 % Sulfuric acid	40 ml
Potassium iodide	15 g
2 3,6-Trimethylquinoxaline	2 g
Water added to	one liter

<Silver bleaching solution composition>

The same composition as the above silver bleaching solution composition was used.

<Fixing solution composition>	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water added to	one liter
(adjusted to pH = 6.0 with acetic acid)	

The color filter thus obtained had square blue portion, green portion and red portion each with one side of 150 μm formed uniformly on the whole borosilicate glass substrate, and no color turbidity was recognized in each color.

When spectral transmittance of each color was measured after the color filter was placed in an oven and maintained at 180 °C for 6 hours, substantially no change was recognized in all of the colors. Particularly the transmittance at 650 nm of the green filter portion, the blue filter portion having the dye formed with a dye developer was not changed at all, whereby excellent heat resistance was confirmed.

Example 2

Color filters were prepared in the same manner as in the above Example 1 except for replacing the cyan dye (Exemplary compound (g)) contained in the light-sensitive silver halide photographic material with Exemplary compounds (c), (e), (i) in the above Example 1.

When the characteristics of the color filters obtained were evaluated in the same manner in the above Example 1, it was confirmed that they had good characteristics.

Example 3

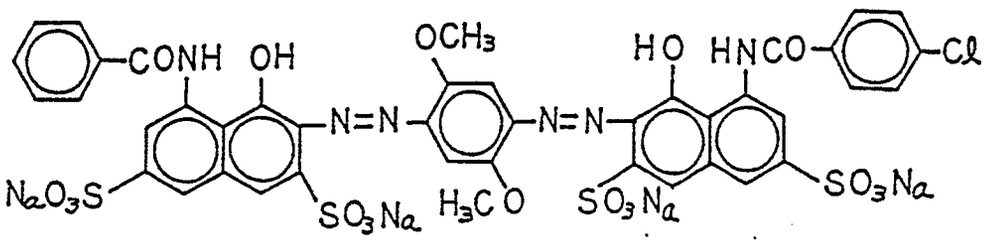
Preparation of silver halide photographic material

A silver iodobromide emulsion containing 4 mole % of silver iodide (average grain size: 0.05 μm, gelatin concentration: 9 % by weight) was prepared by adding an aqueous silver nitrate solution and an aqueous solution containing potassium bromide and potassium iodide at the same time into an aqueous solution containing 10 % by weight of gelatin. The addition conditions were regulated so that Lippman emulsion could be obtained having an average grain size of 0.05 μm.

To the silver iodobromide emulsion thus obtained, 28.3 mg of pentahydrate of sodium thiosulfate per one mole of silver, and the mixture was chemically ripened under the conditions of a temperature of 59.5 °C for 45 minutes.

Subsequently, to the above emulsion were added 1-phenyl-5-mercaptotetrazole and 1-carboxyethyl-3,4,5-hydroxybenzene in amounts of 6×10^{-3} mole and 3.40 g per mole of silver, respectively, and also 15.9 g of the compound SC-1 shown below was added per mole of silver, followed further by addition of H-1 and H-2 used in Example 1 in amounts of 40 mg and 5 mg, respectively per gram of gelatin, to prepare an emulsion coating solution.

Compound SC-1



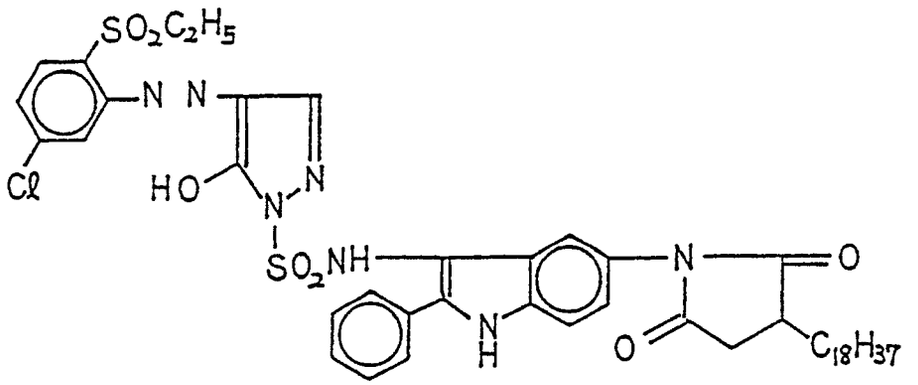
The above emulsion coating solution obtained was applied on a transparent borosilicate glass substrate (30 cm x 30 cm) with a thickness of 1.1 mm to a dry thickness of 3 μm to prepare a photosensitive emulsion layer having a photosensitive emulsion layer. The amount of silver attached was 1.5 g/m^2, and the amount of the dye attached 0.24 g/m^2

This photosensitive emulsion layer has also a backing layer on the surface opposite to that having the above photosensitive emulsion layer in the above borosilicate glass substrate.

Formation of the backing layer is described below.

To an aqueous gelatin solution was added a dispersion of the compound Y-1 shown below, and also the above compounds H-1 and H-2 were added in amounts of 40 mg and 5 mg, respectively. Here, the gelatin amounts previously added were adjusted so that the gelatin in these aqueous gelatin solutions became 5 % by weight. The amount of the compound shown below added into 100 cc of aqueous gelatin solution was 1.35 % by weight.

Compound Y-1



Thereafter, the aqueous gelatin solution was coated on the above borosilicate glass substrate and then dried to form a backing layer. The amount of the above compound Y-1 attached was 10 mg/dm^2.

The above dispersion used was prepared by dissolving 1 g of tricresyl phosphate per 1 g of the compound Y-1 into 4.29 cc of ethyl acetate, then mixing the solution by adding into an aqueous solution containing 0.83 g of gelatin, 2.63 cc of an aqueous solution of 5 % by weight of sodium triisopropyl naphthalene sulfonate and 8.4 cc of water, dispersing by sonication the mixture under the condition of a temperature of 50 °C and removing ethyl acetate, followed further by addition of water to an amount of 17.6 cc.

Preparation of color filter

The method for preparation of a color filter having the mosaic pattern of the three colors of B (blue), G (green) and R (red) as shown in Fig. 2 is to be described below. The size of each picture element is 150 μm x 150 μm.

With a chromium mask for color filter having a square opening with one side of 150 μm being superposed on the above photographic material, the first exposure was effected by use of a tungsten lamp exposure was effected at the position corresponding to the part B in Fig. 2.

The photographic material exposed was dipped in the magenta color developing solution shown below at 25 °C for 3 minutes.

Magenta color developing solution composition	
Magenta coupler 1-(2.4,6-Trichlorophenyl)-3-(p-nitroanilino)-pyrazolin-5-one	2.0 g
Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline•sulfate	1.86 g
Nitrotrimethylenesulfonic acid	3.00 ml
Anhydrous sodium sulfate	6.66 g
0.1 % Aqueous potassium iodide solution	11.00 ml
Anhydrous sodium bromide	0.86 g
6-Nitrobenzimidazole	0.02 g
Sodium sulfite	20.00 g
Hexylene glycol	5.00 ml
Polyethylene glycol	0.60 ml
Diethylhydroxylamine	0.27 ml
Hydroquinone monosulfonic acid	0.10 g
Tertiary butylaminoborane	0.07 g
Sodium thiocyanate	1.00 g
Anhydrous sodium carbonate	16.67 g
Anhydrous sodium hydrogen carbonate	4.00 g

In the above magenta color developing solution, sodium hydroxide was added to adjust the pH value at

27 °C to 12.0.

Next, the photographic material was dipped in a stopping solution (3 % by weight aqueous acetic acid solution) for one minute, then washed with water and bleached by dipping in the silver bleaching solution having the following composition for one minute, followed by washing with water for one minute and drying, to form a blue color portion on the substrate (the first processing).

Silver bleaching solution composition	
Iron ammonium ethylenediaminetetraacetate	200.0 g
Ammonium bromide	10.0 g
Glacial acetic acid	10.0 ml
The solution was made to one liter with addition of water and adjusted to pH = 6.0 with aqueous ammonia.	

Next, on the photographic material after the above processing, another chromium mask for color filter was arranged so that the exposed portion became the part G in Fig. 2 to effect the second exposure.

The photographic material subjected to the second exposure was dipped in the yellow color developing solution having the following composition at 25 °C for 3 minutes, then dipped in the above stopping solution for one minute and washed with water, followed by bleaching, water washing and drying similarly as in the first time to form a green portion on the substrate (the second processing).

Yellow color developing solution composition	
Yellow coupler 2-(p-Carboxyphenoxy)-2-pyvaloyl-2′,4′-dichloroacetanilide	1.5 g
Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline•sulfate	1.86 g
Nitrotrimethylenesulfonic acid	3.00 ml
Anhydrous sodium sulfate	6.66 g
0.1 % Aqueous potassium iodide solution	11.00 ml
Anhydrous sodium bromide	0.86 g
6-Nitrobenzimidazole	0.02 g
Sodium sulfite	20.00 g
Hexylene glycol	5.00 ml
Polyethylene glycol	0.60 ml
Diethylhydroxylamine	0.27 ml
Hydroquinone monosulfonic acid	0.10 g
Tertiary butylaminoborane	0.07 g
Sodium thiocyanate	1.00 g
Anhydrous sodium carbonate	16.67 g
Anhydrous sodium hydrogen carbonate	4.00 g

To the above yellow color developing solution was added sodium hydroxide to adjust the pH value at 27 °C to 12.0.

Next, on the photographic material after the above processing, another chromium mask for color filter was arranged so that the exposed portion became the part R in Fig. 2 to effect the third exposure.

The photographic material subjected to the third exposure was dipped in the red color developing solution having the following composition at 25 °C for 3 minutes, followed by stopping, water washing, bleaching, water washing and drying similarly as in the second time to form a black portion on the substrate (the third processing).

Red color developing solution composition	
Magenta coupler 1-(2,4,6-Trichlorophenyl)-3-(p-nitroanilino)-pyrazolin-5-one	3.00 g
Yellow coupler 2-(p-Carboxyphenoxy)-2-pyvaloyl-2′,4′-dichloroacetanilide	1.00 g
Developing agent 4-Amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline•sulfate	1.86 g
Nitrotrimethylenesulfonic acid	3.00 ml
Anhydrous sodium sulfate	6.66 g
0.1 % Aqueous potassium iodide solution	11.00 ml
Anhydrous sodium bromide	0.86 g
6-Nitrobenzimidazole	0.02 g
Sodium sulfite	20.00 g
Hexylene glycol	5.00 ml
Polyethylene glycol	0.60 ml
Diethylhydroxylamine	0.27 ml
Hydroquinone monosulfonic acid	0.10 g
Tertiary butylaminoborane	0.07 g
Sodium thiocyanate	1.00 g
Anhydrous sodium carbonate	16.67 g
Anhydrous sodium hydrogen carbonate	4.00 g

To the above red color developing solution was added sodium hydroxide to adjust the pH value at 27 °C to 12.0.

Next, on the photosensitive material after the above processing, a chromium mask for color filter was arranged so that the exposed portion became the part R in Fig. 2 to effect the fourth exposure.

The photographic material subjected to the fourth exposure was processed as described below under the condition of a temperature of 33 °C (the fourth processing), whereby the color filter having the mosaic pattern of the three colors of B (blue), G (green) and R (red) was obtained.

Monochromatic developing	1 minute
Stopping	1 minute
Water washing	1 minute
Dye bleaching	1 minute
Water washing	1 minute
Silver bleaching	1 minute
Water washing	4 minutes
Drying	

Here, the baths used for the respective processings had the following compositions.

<Monochromatic developer composition>	
Sodium sulfite	10 g
Hydroquinone	10 g
Potassium hydroxide (48 % aqueous solution)	5 cc
Diethylene glycol	20 cc
Dimedone	0.7 g
Sodium carbonate	20 g
Potassium bromide	2 g
Thiadiazole	0.05 g
Water added to liter	one

<Dye bleaching solution composition>	
96 % Sulfuric acid	40 cc
Potassium iodide	15 g
2,3,6-Trimethylquinoxaline	2 g
Water added to	one liter

After the fourth processing, the photographic material was dipped in the fixing solution having the composition shown below of a liquid temperature of 25 °C or lower for one minute, washed with water for 4 minutes and then dried.

<Silver bleaching solution composition>

The same silver bleaching solution composition as described above was used.

<Fixing solution composition>	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water added to (adjusted to pH = 6.0 with acetic acid)	one liter

For the color filter thus obtained, by use of blue light, green light and red light, respectively, a density of each color picture element was determined by scanning a micro-densitometer (opening scanning area: 250 μm^2).

For the measured density of each color picture element portion, the measurement results when using blue light as the measuring light are shown in Table 1, and the measurement results when using green light as the measuring light in Table 2.

Table 1

	Green light transmissive picture element	Red light transmissitve picture element
Example 3	1.80	1.60

Table 2

	Blue light transmissive picture element	Green light transmissitve picture element
Example 3	1.00	2.00

As is apparent from Table 1 and Table 2, the color filter obtained in Example 3 was confirmed to be excellent in color forming density.

According to the method of the present invention, there can be provided an industrially useful method for preparing a color filter having the following advantages:

(1) Control of the reaction, setting of the conditions of the reaction can be easily done to give excellent production efficiency; and

(2) Besides, a color filter having excellent color reproducibility based on good spectral characteristics, which can be used suitably particularly for such uses as color display or color camera tube can be obtained.

Claims

1. A method for preparing a color filter which comprises forming at least two color picture elements of at least two colors by effecting at least two pattern exposure to a photosensitive emulsion layer formed on a light-transmissive substrate and then developing said pattern exposed portions, characterized in that said photosensitive emulsion layer contains a dye having a silver dye bleaching effect, at least one color picture element of a color is formed by steps of effecting development of said pattern exposed portions according to the silver dye bleaching method which performs the processing for forming a photosensitive emulsion layer containing a dye, the monochromatic developing processing, the silver dye bleaching processing and the silver bleaching processing in this order, and at least one color picture element of other colors is formed by the steps of effecting development of said pattern exposed portions according to the nonincorporated-coupler type color developing method which employs a developer containing a color forming coupler.

2. A method according to Claim 1, wherein said photosensitive emulsion layer contains silver halide.

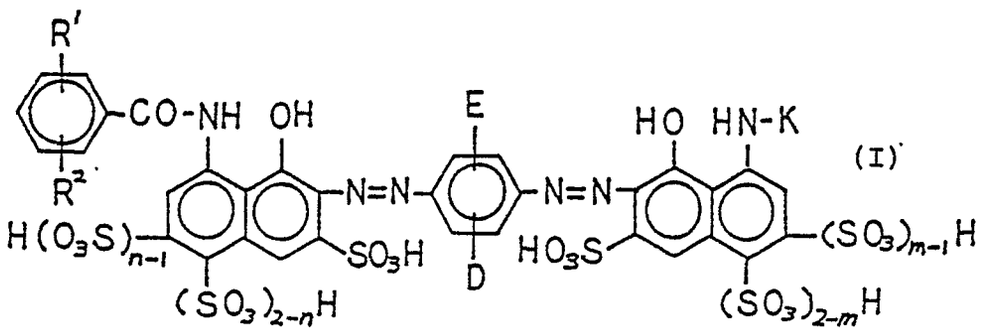
3. A method according to Claim 2, wherein an average particle diameter of said silver halide is 0.1 μm or less.

4. A method according to Claim 1, wherein said photosensitive emulsion layer contains a water-soluble binder.

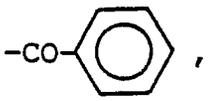
5. A method according to Claim 1, wherein said dye is an azo dye or a phthalocyanine dye.

6. A method according to Claim 5, wherein said azo dye is a bisazo dye.

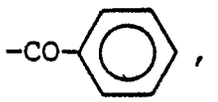
7. A method according to Claim 5, wherein said azo dye is any of combinations of the following formula:



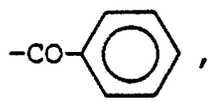
(a) in the above formula (I), compounds wherein R^1 is $-NO_2$, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



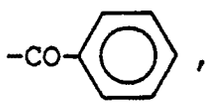
(b) in the above formula (I), compounds wherein R^1 and R^2 are $-NO_2$, D and E are $-OCH_3$ and K is



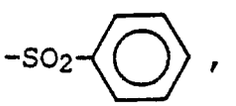
(c) in the above formula (I), compounds wherein R^1 is -Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



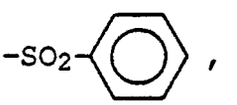
(d) in the above formula (I), compounds wherein R^1 is Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



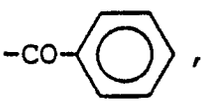
(e) in the above formula (I), compounds wherein R^1 is -Cl, R^2 and D are hydrogen atoms, E is $-OCH_2CH_2OH$ and K is



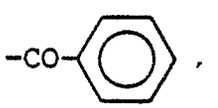
(f) in the above formula (I), compounds wherein R^1 is $-SO_2NH_2$, R^2 and D are hydrogen atoms, E is $-OCH_3$ and K is



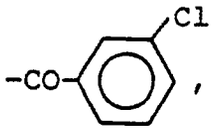
(g) in the above formula (I), compounds wherein R^1 is $-SO_2CH_3$, R^2 is a hydrogen atom, D and E are $-OCH_3$s and K is



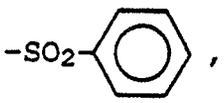
(h) in the above formula (I), compounds wherein R^1 is



R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is

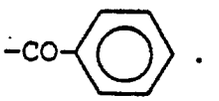


(i) in the above formula (I), compounds wherein R^1 is $-NO_2$, R^2 and D are hydrogen atoms, E is $-OCH_2CH_2OH$ and K is



and

(j) in the above formula (I), compounds wherein R^1 is $-COCH_3$, R^2 is a hydrogen atom, D and E are $-OCH_3$s and K is



8. A method according to Claim 1, wherein a bleaching agent to be used in said dye bleaching processing is a mineral acid or an organic acid.

9. A method according to Claim 8, wherein said mineral acid is at least one selected from the group consisting of hydrochloric acid, sulfuric acid and nitric acid.

10. A method according to Claim 8, wherein said organic acid is at least one selected from the group consisting of sulfamic acid, succinic acid and acetic acid.

11. A method according to Claim 1, wherein said color forming coupler is a ring-opened ketomethylene compound.

12. A method according to Claim 11, wherein said ring-opened ketomethylene compound is acylacetanilide.

13. A method according to Claim 11, wherein said ring-opened ketomethylene compound is 2-(p-carboxyphenoxy)-2-pyvaloyl-2′,4′-dichloroacetanilide.

14. A method according to Claim 1, wherein said color forming coupler is an active methylene compound.

15. A method according to Claim 14, wherein said active methylene compound is a hydrazone or a cyanoacetanilide.

16. A method according to Claim 15, wherein said hydrazine is 1-(2,4,6-trichlorophenyl)-3-(p-nitroanilino)-2-pyrazolino-5-one.

17. A method according to Claim 1, wherein said color forming coupler is a phenol compound or a naphthol compound.

18. A method according to Claim 17, wherein said phenol compound is 2-acetamido-4,6-dichloro-5-methylphenol.

19. A method according to Claim 17, wherein said naphthol compound is N-(O-acetamidophenoethyl)-2-hydroxy-2-naphthoamide.

20. A method according to Claim 1, wherein a subbing layer is provided at the surface of said light-transmissive substrate.

21. A method according to Claim 1, wherein a backing layer is provided on the surface of the above light-transmissive substrate opposite to the surface where the photosensitive emulsion layer is formed.

22. A method according to Claim 1, wherein said silver dye bleaching processing is effected after formation of at least two color portion by repeatedly effecting said pat tern exposure and developing processing due to nonincorporated-coupler type developing method.

23. A color filter formed at least two color picture elements of at least two colors by effecting at least two pattern exposure to a photosensitive emulsion layer formed on a light-transmissive substrate and then developing said pattern exposed portions, characterized in that said photosensitive emulsion layer contains a dye having a silver dye bleaching effect, at least one color picture element of a color is formed by steps of effecting development of said pattern exposed portions according to the silver dye bleaching method

which performs the processing for forming a photosensitive emulsion layer containing a dye, the monochromatic developing processing, the silver dye bleaching processing and the silver bleaching processing in this order, and at least one color picture element of other colors is formed by the steps of effecting development of said pattern exposed portions according to the nonincorporated-coupler type color developing method which employs a developer containing a color forming coupler.

24. A color filter according to Claim 23, wherein said photosensitive emulsion layer contains silver halide.

25. A color filter according to Claim 23, wherein an average particle diameter of said silver halide is 0.1 μm or less.

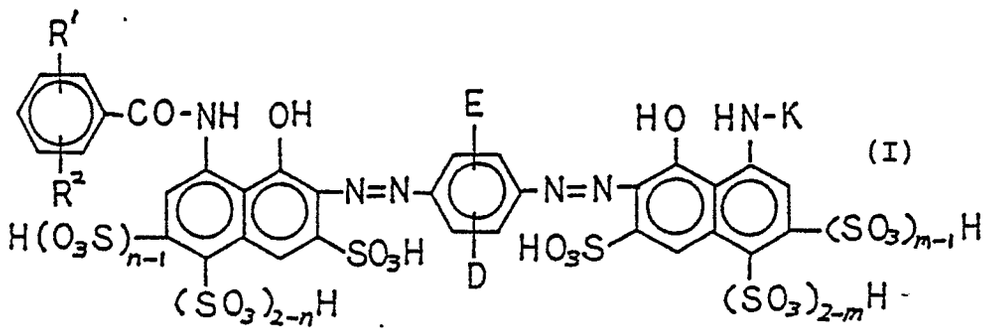
26. A color filter according to Claim 23, wherein said photosensitive emulsion layer contains a water-soluble binder.

27. A color filter according to Claim 23, wherein said dye having a silver dye bleaching effect is a dye.

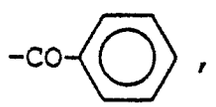
28. A color filter according to Claim 27, wherein said dye is an azo dye or a phthalocyanine dye.

29. A color filter according to Claim 28, wherein said azo dye is a bisazo dye.

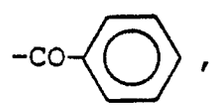
30. A color filter according to Claim 28, wherein said azo dye is any of combinations of the following formula:



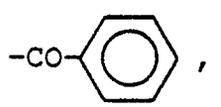
(a) in the above formula (I), compounds wherein R^1 is $-NO_2$, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



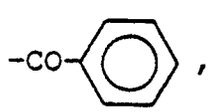
(b) in the above formula (I), compounds wherein R^1 and R^2 are $-NO_2$, D and E are $-OCH_3$ and K is



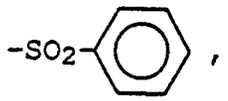
(c) in the above formula (I), compounds wherein R^1 is -Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



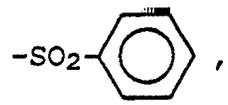
(d) in the above formula (I), compounds wherein R^1 is Cl, R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is



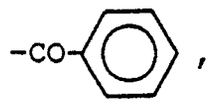
(e) in the above formula (I), compounds wherein R^1 is -Cl, R^2 and D are hydrogen atoms, E is $-OCH_2CH_2OH$ and K is



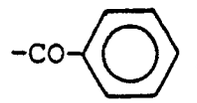
(f) in the above formula (I), compounds wherein R^1 is $-SO_2NH_2$, R^2 and D are hydrogen atoms, E is $-OCH_3$ and K is



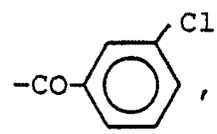
(g) in the above formula (I), compounds wherein R^1 is $-SO_2CH_3$, R^2 is a hydrogen atom, D and E are $-OCH_3$s and K is



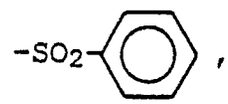
(h) in the above formula (I), compounds wherein R^1 is



R^2 is a hydrogen atom, D and E are $-OCH_3$ and K is

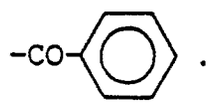


(i) in the above formula (I), compounds wherein R^1 is $-NO_2$, R^2 and D are hydrogen atoms, E is $-OCH_2CH_2OH$ and K is



and

(j) in the above formula (I), compounds wherein R^1 is $-COCH_3$, R^2 is a hydrogen atom, D and E are $-OCH_3$s and K is



31. A color filter according to Claim 23, wherein a dry thichness of said photosensitive emulsion layer is 0.3 to 10 μm.

32. A color filter according to Claim 23, wherein said color forming coupler is a ring-opened ketomethylene compound.

33. A color filter according to Claim 32, wherein said ring-opened ketomethylene compound is

acylacetanilide.

34. A color filter according to Claim 32, wherein said ring-opened ketomethylene compound is 2-(p-carboxyphenoxy)-2-pyvaloyl-2′,4′-dichloroacetanilide.

35. A color filter according to Claim 23, wherein said color forming coupler is an active methylene compound.

36. A color filter according to Claim 35, wherein said active methylene compound is a hydrazone or a cyanoacetanilide.

37. A color filter according to Claim 36, wherein said hydrazone is 1-(2,4,6-trichlorophenyl)-3-(p-nitroanilino)-2-pyrazolino-5-one.

38. A color filter according to Claim 23, wherein said color forming coupler is a phenol compound or a naphthol compound.

39. A color filter according to Claim 38, wherein said phenol compound is 2-acetamido-4,6-dichloro-5-methylphenol.

40. A color filter according to Claim 38, wherein said naphthol compound is N-(O-acetamidophenoethyl)-2-hydroxy-2-naphthoamide.

41. A color filter according to Claim 1, wherein a subbing layer is provided at the surface of said light-transmissive substrate.

42. A color filter according to Claim 1, wherein a backing layer is provided on the surface of the above light-transmissive substrate opposite to the surface where the photosensitive emulsion layer is formed.

FIG. 1

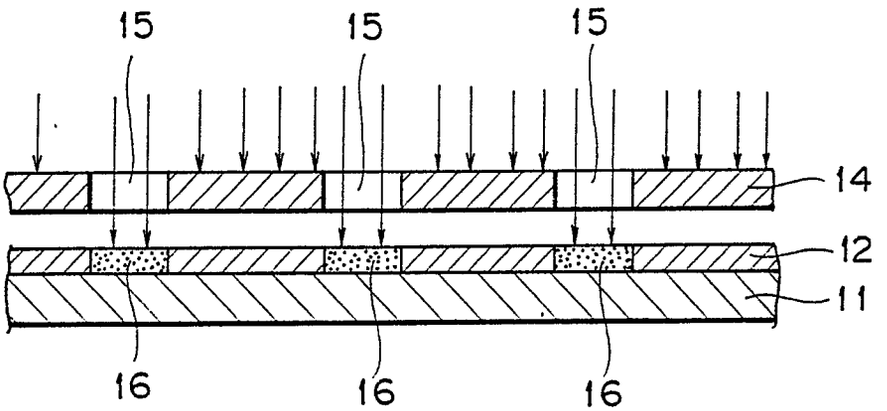

15
15
15
14
12
11
16
16
16

FIG. 2

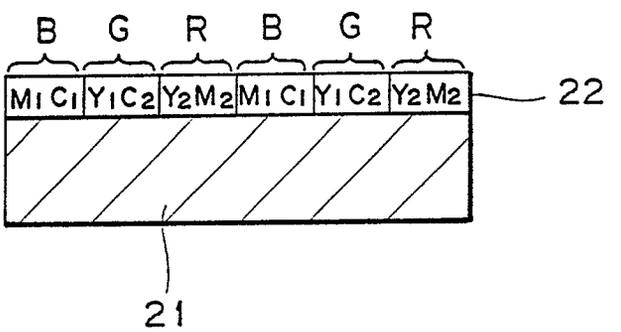

B
G
R
B
G
R
M1 C1
Y1 C2
Y2 M2
M1 C1
Y1 C2
Y2 M2
22
21

FIG. 3

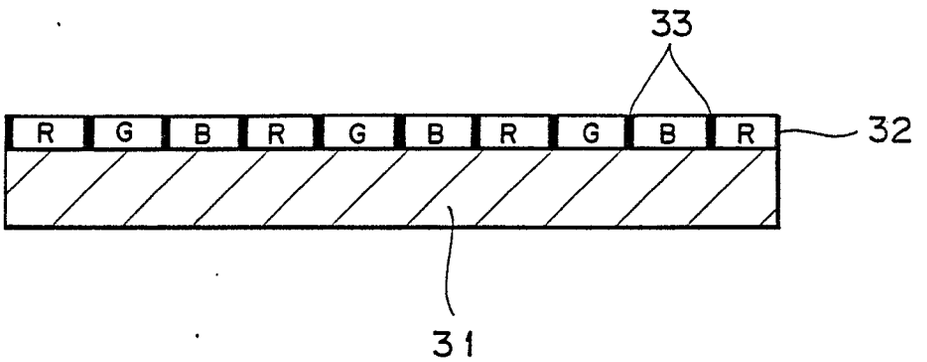


FIG. 4

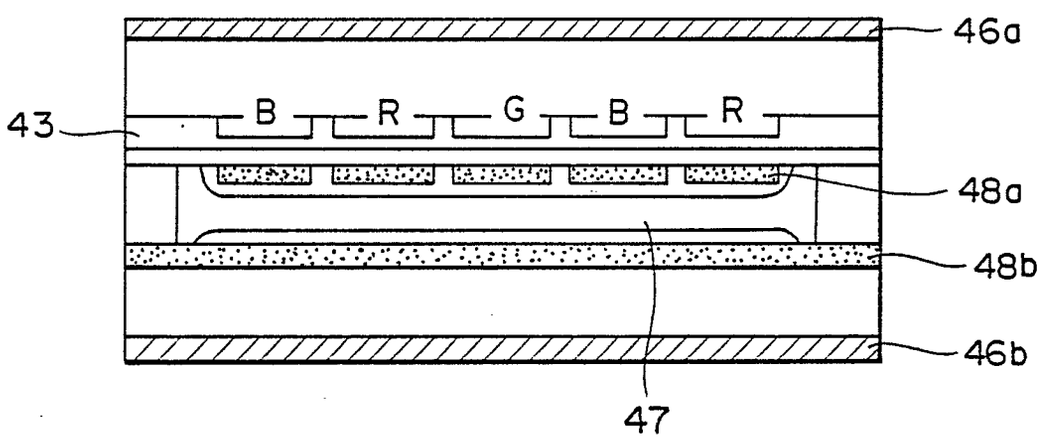
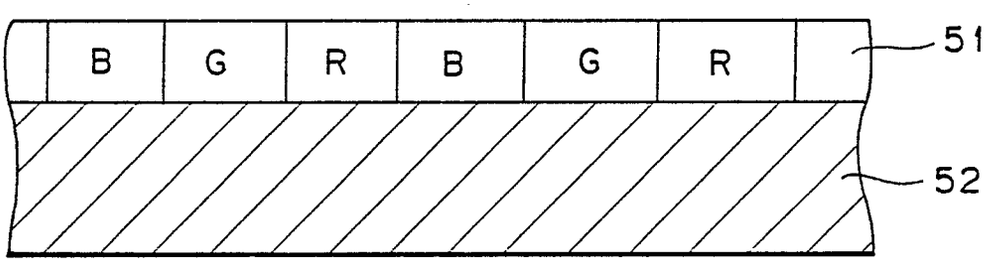


FIG. 5

B	G	R	B	G	R
G	R	B	G	R	B
R	B	G	R	B	G
B	G	R	B	G	R
G	R	B	G	R	B
R	B	G	R	B	G
B	G	R	B	G	R

FIG. 6



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 11 2990

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	DE-A-3 133 164 (FUJI) * Claims; page 23, lines 11-31 *	1-42	G 03 C 7/12 G 03 C 7/28
X,Y	US-A-4 294 900 (AONO) * Examples; claims *	1-42	
X,Y	US-A-4 678 740 (CATANIA) * Claims *	1-42	
X,Y	FR-A-2 251 840 (KODAK) * Claims *	1-42	
Y	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 378 (P-645)[2825], 10th December 1987; & JP-A-62 148 952 (KONISHIROKU PHOTO IND. CO., LTD) 02-07-1987 * Abstract *	1-42	
Y	EP-A-0 233 152 (CIBA-GEIGY) * Page 13, lines 39-49 *	1-42	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	EP-A-0 131 970 (CIBA-GEIGY) * Page 2, lines 2-9 *	1-42	G 03 C 7 G 03 C 5
Y	CH-A- 506 094 (MITSUBISHI) * Column 1, lines 14-31 *	1-42	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-08-1989	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)