



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 1 083 461 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**14.03.2001 Bulletin 2001/11**

(51) Int Cl.7: **G03C 7/30**

(21) Application number: **99202189.9**

(22) Date of filing: **05.07.1999**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(71) Applicant: **Fuji Photo Film B.V.**

**5047 TK Tilburg (NL)**

(72) Inventors:

• **Nauta, Auke**

**5317 JE Nederhemert Noord (NL)**

• **Kashi, Yasuo**

**5045 WG Tilburg (NL)**

• **Hessing, Jacko**

**5121 SV Rijen (NL)**

(74) Representative: **Ottevangers, Sietse Ulbe et al**

**Vereenigde,**

**Postbus 87930**

**2508 DH Den Haag (NL)**

(54) **Digital image forming process and color photographic material for use in this process**

(57) The invention is directed to an image forming process, said process including the development of an exposed color photographic material, which has blue light sensitive layer having yellow dye forming coupler, green light sensitive layer having magenta dye forming coupler, and red light sensitive layer having cyan dye forming coupler, and output of the image information to an output device, wherein said process comprises:

(1) photoelectric reading of the recorded image information on the said developed color photographic material,

(2) conversion of the image information obtained by said photoelectric reading into a digital image infor-

mation,

(3) providing said digital image information with digital image processing so that preferable image characteristics can be obtained, and

(4) output said information on an output device, said color photographic material being characterized in that after development under standard conditions, (5) for the yellow, magenta, and cyan colors the value of the minimum density,  $D_{min}$ , is 0.3 or less, and (6) said color photographic material contains oil-in-water emulsions containing at least one dye forming coupler, at least one of the coupler containing layers has a coupler/oil ratio of 0.01g/g or more and 0.30g/g or less, as well as to a color photographic material for use in this process.

**EP 1 083 461 A1**

## Description

**[0001]** The present invention concerns a method of forming a color photographic image from a silver halide color photographic material (especially, color negative film) and a silver halide color photographic material for this use.

**[0002]** In addition, it concerns the method of forming the color image on an output device, such as a monitor, a projector or a printer, which prints images on the positive material such as color print paper using digital image processing, which is carried out after a developed image is electronically scanned from color photographic material, and color photographic material which is suitable for it.

**[0003]** The color photographic method which is being used most widely now is a so-called negative paper system (hereafter, the N/P system) which prints the image of exposed and developed color negative film on printing paper in color lab and obtains the color print.

**[0004]** This service system is well accepted in the market and is complete, and convenient for the usual customers. In this system the color negative film is developed, the image is obtained, and in the printing exposure to the positive material the color paper prints are obtained in a standard frame size. The color print has been obtained using the printing method, so-called surface exposure.

**[0005]** On the other hand, in recent years, it has also become possible to convert the image information into digital information (after A/D conversion) by scanning the image of the color negative film with a scanner.

**[0006]** In US 5,579,132, it has been disclosed to print on printing paper or to output it to other image media after the digital image is processed. However, the conventional color negative films have been designed to suit the system of the above-mentioned surface exposure method. As a result of the analysis by the inventors of this invention, it has been understood that the photographic characteristic of a conventional color negative film is not optimal for the above-mentioned new digital image processing.

**[0007]** One of the most remarkable results of this invention is a difference of the influence of the mask density. As for a conventional color negative film, because it has a high mask density, the density of the non-image part (called Dmin thereafter) is designed high. Moreover, because the gradation has to be added, the maximum density value Dmax at high exposure amount is close to 4.0. This corresponds to  $10^{-4}$  when converting it into transmittance. The reading accuracy of the scanner decreases when the density value in the image part becomes too high, because the amount of transmitted light becomes too small. Therefore, there is a limit in the transmittance which can be read at high exposure amount.

**[0008]** In the conventional method, in which the digital image processing is not adopted, it is necessary and indispensable to correct the sub-absorption of the color dye by the addition of masking coupler to make the image enough saturated in the color positive material. If the digital image processing is applied, the inventors of this invention discovered that the mask density need not to be raised for masking because the saturation can be improved by the digital image processing.

**[0009]** In case the mask density is low, the concentration difference between the highest density where it can be read with the scanner and Dmin becomes larger. Therefore, the picture taking latitude (synonymous with the dynamic exposure range) which can reproduce the gradation on the color positive material increases.

**[0010]** The density as used herein is a photographic density, and it is synonymous with the optical density. Moreover, the explanation of masking is added here. In the color negative film, for example, the magenta dye which is produced as a result of the color development of the magenta coupler has the sub-absorption also in the vicinity of 440 nm besides absorption in the vicinity of 550 nm which is originally necessary. It causes to decrease the saturation of the color print image. As countermeasure, a magenta coupler (that is, mask coupler) with the releasing group (coloring group which contains the arylazo group) which has absorption in the sub-absorption spectrum area, is added to the color negative film.

**[0011]** The dye generated from the magenta coupler by the color development increases also the density by the sub-absorption in the vicinity of 440 nm as well as the main absorption. This density increase is compensated by a decrease (reduced concentration) in optical absorption in the same spectrum area which is caused by the releasing group of the mask coupler. As a result, the color mixing due to the sub-absorption is masked. This was a compensation mechanism, and the masking was indispensable in the N/P system of the usual method.

**[0012]** The reading accuracy of the scanner on the high density side decreases when the density value exceeds 3.0 due to the poor transmittance signal to noise ratio. This accuracy error is reflected in the highlight part of the print. In the final print, because the highlight part exerts an important influence on the picture quality, an important part of the print quality will receive an adverse effect.

**[0013]** Therefore, it is necessary to read information recorded in the color negative film precisely, and it is required that Dmax is lowered to such levels that it would be possible to read precisely within the range of the exposure latitude.

**[0014]** The color negative film was designed on the assumption of being printed out to the positive material directly by the surface exposure method as described above. Therefore, it is not necessarily designed optimally for the new method which digitalizes its scanned image information and outputs it to various prints and other media's.

**[0015]** It is accompanied by the defect of the picture quality in the highlight part etc. due to the reading accuracy deterioration of scanner.

**[0016]** In US 5,579,132, JP-A-10-111548, and JP-A-10-20457, it is disclosed to print on printing paper or to output to other image media after the digital image is processed. US 5,579,132 discloses a process which includes the image exposure on a color photographic material, the development, the photoelectrical image reading, the image processing, and the output to color photographic paper. These processes can provide an excellent digital photographic image with good sharpness, granularity, and color reproduction. The picture taking photographic material in this application preferably has a special spectral sensitivity and does not include a masking coupler and DIR coupler.

**[0017]** JP-A-10-111548 discloses a color negative film which has a special spectral sensitivity, with which one can get a excellent digital photographic image with good sharpness and granularity.

**[0018]** JP-A-10-20457 discloses a color negative film which has Dmin value less than 0.2 and special gradations of the blue sensitive photographic layer, green sensitive photographic layer, and the red sensitive photographic layer, with which one can get a excellent digital photographic image with high productivity.

**[0019]** During the research of a suitable color negative film for this digital processing, it was noticed that the granularity in the under exposure condition (the exposure amount is lower than the normal exposure condition) was often unsatisfactory. The picture is taken in a wide exposure range from the under exposure to the over exposure condition (the exposure amount is more than the normal exposure condition). In wide exposure area, it is necessary to obtain a output image of good quality, and the necessity of the improvement of the granularity especially in the under exposure was noticed. When the digital image processing was done, the deterioration of granularity was more remarkable than that in the conventional print method by a usual surface exposure.

**[0020]** The foot part of the gradation curve of the color negative film will be used in this case, where it has a soft gradation. The dependence of the developed color negative film density on the incident light amount becomes small in this region. Therefore, it is necessary to expand the concentration information more than the case in the normal exposure to obtain the output image with an enough picture quality.

**[0021]** For example, assuming that, in the normal exposure level, the change of 1.0 in the log value of the incident light amount causes the density difference of 0.8 on the developed color negative film, it might happen that the change of 1.0 in the log value of the incident light amount causes the density difference of 0.2 on the developed color negative film in the under exposure, because the gradation is soft in the under exposure region.

**[0022]** When the density of the developed color negative film is photoelectronically read, after some image processing, those information is output to a color photographic material, it is necessary to expand the density by  $1.0/0.8=1.25$  in the normal exposure area, because the density difference of about 1.0 on the output color photographic material is needed for the change of 1.0 in the log value of an incidence light amount on a picture taking material.

**[0023]** On the other hand, the expansion of  $1.0/0.2=5.0$  is needed in the under exposure area.

**[0024]** The granularity is a microscopic density distribution. This density difference is detected by the photoelectronical reading means. This microscopic density difference will be expanded as shown in above. It turned out that the granularity in the output image became more remarkable, because this expansion rate is larger in the under exposure area.

**[0025]** In case of the conventional color negative film, much of so-called DIR (development inhibitor releasing) compounds is used mainly in order to control the inter layer effect for the color reproduction. It is well known that this compound shows not only the enhancement of interlayer effect but also the granularity improving effect, because of its development inhibiting effect. However, because the color reproduction can be controlled by the digital image processing in the color negative film of this invention, it is desirable not to use the DIR compound from the cost point of view. Therefore, it was hoped to prevent the granularity deteriorating in case of no use of DIR compounds.

**[0026]** In JPA11-65051, it is disclosed that competitive compounds are introduced in a image formation process which is designed for the digital image processing in order to improve its granularity. The competitive compounds mean those which can react with the oxidized color developing agent competitively against the dye forming coupler. This competitive compounds are added in a color developing solution or in the color photographic material. Although this is a good method, but if this compound is added in a color developing solution, this developing solution would be different from one available in the market, which would restrict a wide use.

**[0027]** Moreover, it is necessary to contain more amount of couplers, because the amount of formed dye may decrease when competitive compounds are used in the photographic image formation process.

**[0028]** The method of improving granularity is also disclosed in JPA11-109583 in the color negative film designed for the digital image processing. In this case, also the specially designed developing solution should be used and the application would be limited.

**[0029]** The inventors of this invention come to notice the granularity improvement is important, especially in the under exposure area, and finally came to this invention.

**[0030]** This invention is accordingly directed to an image forming process, said process including the development of an exposed color photographic material, which has blue light sensitive layer having yellow dye forming coupler,

green light sensitive layer having magenta dye forming coupler, and red light sensitive layer having cyan dye forming coupler, and output of the image information to an output device, wherein said process comprises:

- (1) photoelectric reading of the recorded image information on the said developed color photographic material,
- (2) conversion of the image information obtained by said photoelectric reading into a digital image information,
- (3) providing said digital image information with digital image processing so that preferable image characteristics can be obtained, and
- (4) output said information on an output device, said color photographic material being characterized in that after development under standard conditions,
- (5) for the yellow, magenta, and cyan colors the value of the minimum density,  $D_{min}$ , is 0.3 or less,
- (6) said color photographic material contains oil in water emulsions containing dye forming coupler, at least one of the coupler containing layers has a coupler/oil ratio of 0.01g/g or more and 0.30g/g or less.

**[0031]** The invention also relates to a process wherein the image is output to an output device, preferably by printing on a silver halide color photographic paper and to a color photographic material for picture taking for use in the above-described process.

**[0032]** This invention involves the method of forming the color image characterized by development after picture taking, digitalization of the obtained image, digital image processing, image output, and the color photographic material used for this method. The most suitable color photographic material for this invention is a color negative film.

**[0033]** The following descriptions are mainly written for the color negative film, however, it is to be understood, that other systems may be applied without deviating from the gist of the invention, as will be apparent to the skilled person.

**[0034]** The explanation on those components is as follows.

**[0035]** First of all, in order to improve the granularity, it is necessary to reduce the coupler/oil ratio. In this invention, the term "oil" means the organic solvent with a high boiling point, which can dissolve the dye forming couplers.

**[0036]** Examples of the high boiling solvent used in the present invention are described in U.S. Pat. No. 2,322,027.

**[0037]** There can be given examples of the high boiling organic solvent which can be used in the above oil-in-water dispersion method, phthalic acid esters (for example, dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-tert-amylphenyl)isophthalate, and bis(1,1-diethylpropyl)-phthalate), phosphoric acid or phosphonic acid esters (for example, diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldiphenyl phosphate, dioctylbutyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, and di-2-ethylhexylphenyl phosphate), benzoic acid esters (for example, 2-ethylhexyl benzoate, 2,4-dichlorobenzoate, dodecyl benzoate, and 2-ethylhexyl p-hydroxybenzoate), amides (for example, N,N-diethyl dodecanamide and N,N-diethyl laurylamide), alcohols or phenols (for example, isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic esters (for example, dibutoxyethyl succinate, di-2-ethylhexyl succinate, 2-hexyldecyl tetradecanate, tributyl citrate, di-ethyl azelate, isostearyl lactate, and trioctyl citrate), aniline derivatives (for example, N,N-dibutyl-2-butoxy-5-tert-octylaniline), chlorinated paraffin (for example, paraffins having a chlorine content of 10 to 80%), trimesic acid esters (for example, tributyl trimesate), dodecylbenzene, diisopropylnaphthalene, phenols (for example, 2,4-di-tert-amylphenol, 4-dodecylphenol, 4-dodecyloxycarbonylphenol, and 4-(4-dodecyloxyphenylsulfonyl)phenol), carboxylic acids (for example, 2-(2,4-di-tert-amylphenoxy)butyric acid, and 2-ethoxyoctanedecanoic acid), and alkylphosphoric acids (for example, di-2-(ethylhexyl)phosphoric acid and diphenylphosphoric acid). Further, there may be used in combination as an auxiliary solvent, an organic solvent having a boiling point of 30°C, or higher and about 160°C or lower (for example, ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate, and dimethylformamide).

**[0038]** The coupler is contained in the oil-in-water emulsion in this invention. In at least one coupler containing layer of the color negative film used in this invention, the ratio of Cp/Oil is 0.01~0.30g/g, and, preferably, 0.01~0.15g/g. The coupler is dissolved in oil, and distributed in the emulsion containing layers in a color photographic material. In case the Cp/Oil ratio is small, the coupler exists in more number of oil droplets, and will be distributed more uniformly in the photographic material. Therefore, the density distribution becomes more uniform after the color development, and excellent granularity can be obtained.

**[0039]** It is preferable to use this technology in the highest sensitivity layer in each color sensitivity layer which has an important role on the granularity when exposing the material in the under exposure condition. Moreover, it is preferable to use this technology in the green sensitive layer which plays the most important role visually.

**[0040]** Next, the design of the color negative film of this invention is explained, in which the density in the non-image part is explained.

**[0041]** As mentioned before, the masking is designed in the non-image part of the conventional color negative film. The red, green, and blue density of the non-image part for the conventional color negative film is designed to be about 0.2-0.3, 0.7-0.8, and 0.9-1.0 respectively. It decreases the amount which corresponds to the sub-absorption contribution of the generated dye in the image part. Excellent color reproduction is usually obtained by making amendment for the

sub-absorption density.

**[0042]** For this invention the minimum density ( $D_{min}$ ) of the non-image part should be 0.3 or less for red and green and blue color.

**[0043]** In this invention, it is preferable that highest density ( $D_{max}$ ) of color negative film is 1.0 or more. The scanner reading accuracy deteriorates when it is too high. Therefore, more preferably it is 1.0 or more and 3.5 or less. According to a more preferred embodiment the value is 1.0 or more and 3.0 or less, and in the most preferred embodiment it is 1.0 or more and 2.5 or less. As a result, the exposure latitude can be secured.

**[0044]** One of the means to decrease the density of the non-image part ( $D_{min}$ ) is to decrease the amount of masking coupler in the color negative film. It is preferable to add no masking coupler. Of course, lowering the mask level decreases the saturation of the color image, and is accompanied by an increase of the color mix and a decrease in the color reproducibility. This problem can be solved by the adoption of the digital image processing after the image information is scanned in this invention; the software parameters in the digital image processing can be selected such that the proper color mix and color reproduction is obtained. Therefore, an extreme reduction of mask coupler becomes possible.

**[0045]** In order to reduce the  $D_{min}$  value, it is also a good mean to add some hydroquinon derivatives which can react with the oxidized color developing agent in the color negative films. Addition of these compounds in non-light sensitive layers is also effective, but the addition in the light sensitive layers, which means the layers containing silver halide emulsion, is especially effective.

**[0046]** The density of the non-image part originates also from the spectral sensitizer which remains without being washed out, irradiation dye added by purposes such as irradiation prevention and filters, colored processing agent not washed out, the fog of the silver halide emulsion and the colored reaction product besides the mask density on the film. By minimizing these factors and /or reducing the amount of silver halide emulsion coating, it is also possible to reduce the  $D_{min}$  value. The contribution of the mask density is very high in the conventional color negative film, so the less or no usage of the mask coupler in our invention has a major reduction in the density of the non image part.

**[0047]** Next the color photographic material of this invention preferably has the following gradation. When the characteristic curve is shown in a rectangular co-ordinate system, whose vertical axis shows the transmittance of the said developed photographic material and the horizontal axis shows the logarithm of the light exposure,

the point A on the characteristic curve is defined at a transmittance of ( $T_{max} - 0.03$ ), ( $T_{max}$  is the maximum transmittance of the said developed photographic material).

$E_a$  is defined as the value of logarithm of the light exposure at the point A,

the point B on the characteristic curve is defined at a transmittance of ( $T_{min} + 0.03$ ) ( $T_{min}$  is the minimum transmittance),

$E_b$  is defined as the value of logarithm of the light exposure at the point B,

the transmittance value which corresponds to  $(E_a + E_b)/2$  on the straight line AB is defined as  $T_0$ ,

and the transmittance value which corresponds to  $(E_a + E_b)/2$  on the said characteristic curve is defined as  $T_1$ ,

the design of the color negative film which is characterized by the value  $T_1 - T_0$  of -0.15 or more and 0.3 or less is preferable.

**[0048]** In this case, we realized more accurate gradation of the highlight in the color print. First, we will explain the method to obtain the characteristic curve and  $D_{min}$  ( $T_{max}$ ).

**[0049]** A color negative film is exposed through the spectrally neutral carbon wedge (density inclination 0.8/cm). In this case, the standard light source (in conformity with International Standard (ISO 5800)) for deciding the sensitivity of the color negative film is used. Then, CN16(Fuji Photo Film Co., Ltd.) was used for processing. This processing condition is one of the internationally common processing condition according to the above-mentioned International Standard as well as C41(Eastman Kodak) and CNK4(Konica Corp.). Then, the yellow density of this film is measured using the light which comes through the filter whose transmittance maximum is at 483 nm, the magenta density is measured using the light which comes through the filter whose transmittance maximum is at 547 nm, and the cyan density is measured using the light which comes through the filter whose transmittance maximum is at 689 nm. Using this method, the characteristic curve is obtained.

**[0050]** Fig. 11 is a characteristic curve of a conventional color negative film, whose vertical axis shows the density.

**[0051]** Taking the red sensitive emulsion layer R as an example, the following explanation may be given.

**[0052]** The characteristic curve of R was shown in Figure 12 by the optical density and the transmittance. The gradation is designed to become a straight line almost, when the optical density is plotted in the vertical axis as for a conventional color negative film.

**[0053]** When the density is converted into the transmittance, it becomes a reverse-S shape curve. In the high exposure region, the change in the transmittance according to a change in the exposure becomes very small.

**[0054]** The detection device used for the scanner converts it into the digital information according to the incident light

energy. Because the changes in the transmittance are small in this area, the error of reading is large. It was not possible to expect good accurate gradation reproduction. On the other hand, in this invention we make the characteristic curve shown in Figure 13. As a result, there is enough transmittance change over a wide exposure latitude range, and a bigger transmittance change in the high exposure area (in the highlight area in color print).

**[0055]** This invention shows that the sufficient reading accuracy is obtained even in the high density area where usually the reading accuracy of the scanner becomes deteriorated. Consequently, accurate gradation results in the color prints are obtained. The characteristic curve of this invention can be obtained with technological means, which are common for an usual engineer in this industry.

**[0056]** That is, the exposed layer is made to be a composition of more than two layers, one layer is made to be of high sensitivity, and a silver halide emulsion with soft gradation is used here. Or, more than two kinds of silver halide emulsions with different sensitivity are mixed.

**[0057]** As a result, the emulsion layer which is responsible for this high sensitivity area has a soft gradation characteristics. In case of no use of coupler or use of limited amount of coupler in this layer, very soft gradation characteristics can be obtained. On the other hand, another layer takes charge of the exposure area of low sensitivity, in which the silver halide emulsion has a high gradation characteristics. In order to make the gradation of the silver halide emulsion more hard, the method to make monodispersed emulsion particle can be adopted, for example. In case of high amount use of coupler, very hard gradation characteristics can be also obtained.

**[0058]** Moreover, it is preferable for the cyan, magenta, and yellow coupler to reduce weight as much as possible and to decrease the coated quantity of the silver halide. It is preferable to make the coated amount of silver halide on the color negative film to be 0.5-8.0 g-Ag/m<sup>2</sup>.

**[0059]** In this invention, the image information output from the color negative film is digital image information. The output device, which outputs the image information can be any suitable output device, such as a computer monitor, a projector and as preferred embodiment, a printer. The printer which inputs the image information to the color positive material can be any positive image printing device which inputs digital information.

**[0060]** Preferable color positive material is the silver halide photographic material such as a silver halide color printing paper, a color diffusion transcript material (color instant photograph), and a heat developing type color diffusion transcript material (Pictography made by Fuji Photo Film Co., Ltd.), non silver photographic material such as inkjet, sublimation dye transcript recording material, heat developing multi-layer material for instance "Thermo auto chrome(Fuji Photo Film Co., Ltd.)".

**[0061]** The silver halide color paper is most preferable.

**[0062]** Regarding the process in which the image information is read from the film, it is digitalized, the digital image processing is done, and output to the positive image, the explanation will be given using examples.

I. Outline of flow in device with which method of forming image of this invention is done

II. Picture reproducer

1. Image information reading from film which has been developed

2. Image processing of image information

3. Output of processed image signal to an output device

III. Positive material for output

IV. Color picture taking material (color negative film)

V. Processing

I. Outline of flow in processing with which method of forming image of this invention is done.

**[0063]** Fig. 1 shows the image processing device used for this invention and the flow of operation of the method of forming the image of this invention.

**[0064]** In the processing equipment of this invention, it is preferable that there is a means to detect the kind of the exposed color negative film (It is called the film thereafter) at the start of the process, though it is not a composition required in the invention. The film is taken from the left end of this diagram into processing equipment. First of all, the kind of the film is read (01). It is detected whether it is the film which suits the method of forming the image of this invention, in a word, a low mask density, or a film of the usual. The image processing condition thereafter is set based on this. The processing is done here. This condition can be the above-mentioned common international processing. (Concretely, above-mentioned C41, CN16, and CNK4, etc., substantially almost common processing for International Standard ISO5800). Moreover, it can be the rapid processing shown in JPA 6-51479 etc. The fundamental image processing conditions are the same for the usual film and the film of this invention.

**[0065]** It is preferable to be able to choose the operation condition setting in the image processing device by the

detection result of each film because  $D_{min}$ .

**[0066]** The detection of the kind of the film can be done using the punch sign for the identification which is called DX code recorded on the film.

**[0067]** Moreover, the operator occasionally does the selection operation according to a predetermined standard regardless of what the DX code is. (04). Or, if it is a dedicated device to which only this invention method is done, the selection of such detection and the condition is needless.

**[0068]** Moreover, the processing of the film of the usual and the processing of the film of this invention can be done with one device by detecting the kind of this film.

**[0069]** The film is transported in a series of processing tanks in the developing machine. Next, the film to which the color development, the bleaching, fixing, washing or stabilization is performed moves to image information reading device (1).

**[0070]** The density of each minute area unit (It is called the pixel usually) which composes the image of the film is measured and the image information is read as a density of each pixel.

**[0071]** The image information is converted into a electric picture signal, and, converted into the digital signal by A/D (analogue/digital) transducer 18 through amplifying device 17.

**[0072]** After the correction due to the CCD function, such as the sensitivity difference of each pixel and dark current etc., this information signal is sent to image processing device 5 through log converter 20. In the image processing device, the electrical treatment is added to the image information.

**[0073]** The signal obtained from the film of this invention is converted into the digital image signal with a picture quality similar or better than that obtained from the film with a standard gradation and standard  $D_{min}$ .

**[0074]** The feature in this invention is to be the correction of photographic characteristic by the image processing. The image processing operation described here is separately applied for as the Japanese patent application No. 8-174022 and No.8-182551.

**[0075]** The picture signal is output to an output device (8), and as a result the positive image is obtained.

**[0076]** Every kind of output device, which inputs a electric picture signal is acceptable. Especially, a preferable output device is a printer for the silver halide color print (color print, instant photograph, and heat developing type color diffusion transcript type, etc.), ink jets, the heat sensitive transcript material of sublime type, and the heat sensitive transcript material of wax type, etc.

**[0077]** This invention method of obtaining a positive image from the film of this invention and the outline of the device were described above. Details are explained further as follows.

**[0078]** When converting the image obtained from the film used for this invention into the characteristic value of the photograph for the output by the image processing, it is meant to obtain the image information whose image quality is comparable with the image information obtained by developing a standard usual color negative film. Concretely, though it is basic to judge the image quality by the observation of the photographic image, when the objectivity is valued, the image density can be used as a characteristic value.

**[0079]** More concretely, it can be said that the comparable image quality to the standard processing is obtained if the density value is within  $\pm 10\%$  of reference.

**[0080]** It can be judged that because the amount of the one key correction of the color printer in a usual surface exposure method is about 8%, the characteristic difference within 10% is allowed.

## II. Picture reproduction device

**[0081]** The process of the image information reading of the film of this invention and the digitization and the output to the printer for the positive image are explained in the following paragraph.

**[0082]** We explain it here using a picture reproduction device shown in the Japanese patent application No.8-174022 and 8-182551.

**[0083]** However, neither the processing equipment of this invention nor the method of the image reproduction are limited to this.

**[0084]** Fig. 2 is a block diagram which shows a basic composition of the image reproduction system by this invention. The image reproduction system has the following as shown in Fig. 2.

**[0085]** Image reader 1 which generates digitalized image data, reading color image. Image processing device 5 which gives image processing to image data generated with image reader 1. And, image output device 8 which reproduces the color image based on image data on which the image processing is given with image processing device 5.

### 1. Image information reading from film

**[0086]** The image reading can be mainly done by the following three methods.

(i) The film is wrapped around the rotation drum. The drum is rotated while irradiating measuring beams combined with the color separation filter. Vertical scanning is done in the direction of the drum at the same time and the reflection density of each pixel is photoelectronically detected by the photomultiplier. This is read as a electric information and amplified.

(ii) Line CCD-scanning method which receives transmission density or reflection density from line CCD which displays receiving element to one-dimension. While sub-scanning the image on film, it converts the image into electric information

(iii) Area CCD method which reads density of pixel by two dimension, and converts it into electric information and permute pixel density of the area CCD in time series by electric scanning. You can even adopt either. Especially, the preferable one is an area CCD method.

**[0087]** This invention can be executed without any trouble by the other two methods, though the explanation thereafter is given on the assumption of this method.

**[0088]** Moreover, the reading of image information can adopt the reflection density reading method from the film.

**[0089]** External appearance of the image reproduction system of Fig. 2 are shown in Fig. 3. In an actual image reproduction system, the image reader 1 can selectively connect the reflection type image reader 30 which reads the color image recorded in color print or the transmittance type image reader 10 which reads the color image recorded on the film with image processing device 5. As a result, both of the color image recorded on the color print and on the film can be reproduced.

**[0090]** The image reader is explained here for the color negative film which relates this invention.

**[0091]** Fig. 4 is a schematic drawing of transmittance type image reader 10 for the color image reproduction system. As shown in Fig. 4, transmittance type image reader 10 can read the color image photoelectronically by irradiating light to the color image on film F, and detecting light which is transmitted. This is provided with the following. Light energy adjustment unit 12 from source of light 11, color separation unit 13 to decompose original light from source of light 11 into three colors of R (red), G (green), and B (blue), diffusion unit 14 which diffuses light to be irradiated to film F flat, CCD area sensor 15 which detects light by which film F is transmitted, and the electric zoom lens 16 with which light which the transmitted film F is focused in CCD area sensor 15.

**[0092]** This transmittance type image reader 10 can read many kinds of films like 135 negative films and 135 positive films advanced photo system (APS) film etc. by exchanging the film carrier not shown in the figure.

**[0093]** Halogen lamp is used as the light source 11. As for light energy adjustment unit 12, the light energy can be changed by moving two throttle plate.

**[0094]** The color separation unit(13) rotates a disk containing three filters, B, G, R, and decomposes light into three colors.

**[0095]** Moreover, CCD area sensor 15 possesses the light receiving element of 920 pixels in length and 1380 pixels in width, and can read the image information on the film in the high-resolution evaluation.

**[0096]** CCD area sensor 15 forwards the image data of the even number field and the image data of the odd number field one after another.

**[0097]** In addition, the transmittance type image reader 10 has the following. Amplifier 17 which amplifies picture signal of R, G, and B, analog to digital converter 18 in which picture signal is digitalized, CCD correction means 19 to give the correction due to the difference of sensitivity of each pixel and dark current to the picture signal, and, log converter 20 which converts the image data of R, G, and B into the density data.

**[0098]** Log converter 20 is connected with interface 21.

**[0099]** Film F is maintained in carrier 22. It is sent to a fixed position by driving roller 24 driven by motor 23. It is press-hold in the stopped state. When the reading of the color image of one scene is completed, one scene is sent. As for an auto carrier to handle the negative film, the one used in the usual mini lab, such as NC135S made by Fuji Photo Film Co., Ltd., can be used. The image which corresponds to the full size, the panorama size, and the power size, etc. can be read. Moreover, when a trim carrier in the mini lab is used, the enlargement of 1.4 times becomes possible. Moreover, as for a reversal carrier the one indicated in the Japanese patent application 7-275359, 7-277455, 7-285015, No.7-271048, and 7-275358 can be used.

**[0100]** Moreover, the frame detection sensor 25 detects the concentration distribution of the color image recorded on film F. It outputs the detected density signal to CPU26 which controls transmittance type image reader 10. CPU26 calculates the frame position of the color image recorded on film F based on this density signal. It stops the drive of motor 23 when it judged that the frame position of the color image reached a fixed position. You can set up the image reading device at any place, such as an exit of dryer part of the processor, a independent reading position, and the image processing devices or printers.



## 2. Image processing

**[0101]** Image reader 1 shown in Fig. 1 and Fig. 2 was explained in detail above. Next, the image processing device 5 (shown in Fig. 1 and Fig. 2) is explained.

**[0102]** Fig. 5 and Fig. 6 show the block diagram of the composition of the image processing device 5. As shown in these Figures, the image processing device 5 is made up of interface 48 which can be connected with interface 21 of the transmittance type image reader 10 or interface 41 of the reflection type image reader 30. It is provided with the following. The arithmetic operation means 49 which add the value of two adjoining pixel data of each line, average, and make one pixel data, the first line buffer 50a and the second line buffer 50b by which the pixel data in each line is alternately memorized, the first, second, and third frame memory unit 51, 52, and 53 which memorize image data corresponding to color image of film F (Fig. 4).

**[0103]** The first line buffer 50a and the second Line buffer 50b memorize the pixel data of the line of odd number and even number alternately.

**[0104]** In execution, first of all, the first reading (Hereafter, it is called pre-scan) with the image reader 1 is done to the color image of one scene recorded on film F. Afterwards, the read image is converted into the digital image data. Based on the image data obtained by this pre-scan, the condition of second reading will be set by the image processing device 5 (Hereafter, it is called real-scan). And, based on the readout condition, the real-scan is executed, and the digital image data which will have the image processing is obtained. To do this processing, the image processing device 5 memorizes the image data obtained by the pre-scan in the first frame memory unit 51.

**[0105]** The image data obtained by the real-scan is memorized in the second frame memory unit 52 and the third frame memory unit 53.

**[0106]** These frame memory units are explained in detail before other components shown in Fig. 5 and Fig. 6 here are explained.

**[0107]** Fig. 7 is a block diagram which shows details of the 1st frame memory unit 51 and the 2nd frame memory unit 52 and the 3rd frame memory unit 53.

**[0108]** As shown in Fig. 7, the image processing device 5 has the following.

**[0109]** The 1st frame memory unit 51 and the 2nd frame memory unit 52 and the 3rd frame memory unit 53 are provided with R data memory 51R, G data memory 51G, and B data memory 51B, which memorize image data corresponding to R(red), G(green), and B(blue), R data memory 52R, G data memory 52G, B data memory 52B, R data memory 53R, G data memory 53G, and B data memory 53B respectively to process image data.

**[0110]** The image data obtained by the pre-scan is memorized in the first frame memory unit 51 as the above-mentioned.

**[0111]** Image data which is obtained by the real-scan is memorized in the 2nd and 3rd frame memory unit 52.

**[0112]** As for Fig. 7, the state that the image data of the pre-scan is input to the first frame memory unit 51 from the input bus 63, and the image data of the second frame memory unit 52 is output to power output bus 64 is shown.

**[0113]** The composition of the image processing device 5 is explained again based on Fig. 5 and Fig. 6. Image processing device 5 is provided with CPU60 which controls the whole image processing device 5. CPU60 can communicate with CPU26 (Fig. 4) which controls transmittance type image reading device 10 and via a communication line (is not shown in the figure). And, it is possible to communicate with CPU which controls image output device 8 described later.

**[0114]** By this composition, based on the image data of the pre-scan memorized in the first frame memory unit 51, CPU60 will change the real-scan condition of image reading.

**[0115]** In addition, if necessary it can change the image processing condition given to the image.

**[0116]** That is, based on the image data obtained by the pre-scan, so as to use dynamic range of CCD area sensor 15 or CCD line sensor 35 efficiently in the real-scan, CPU60 determines the condition of real-scan. It outputs the readout control signal to CPU26 of transmittance type image reading device 10 or to CPU46 of reflectance type image reading device 30 (this is not related to this invention).

**[0117]** In this case, when this readout control signal is input, CPU26 of the transmittance type image reading device 10 (or, CPU46 of the reflecting image reading device 30) controls the light intensity and the accumulation time of CCD area sensor 15 or CCD line sensor 35, which can be adjusted with light quantity adjustment unit 12 or 34.

**[0118]** Based on the obtained image data, CPU60 outputs the control signal to the image processing means, so as to reproduce the best color image which has the best density, gradation and color on the color paper.

**[0119]** In this case, the image reading condition and the image processing condition (which is decided by CPU60) are memorized in memory 66.

**[0120]** When the operator's instruction is hold, CPU60 does not decide the condition based on the above-mentioned pre-scan image data and control and input various signals based on the kept condition. The operator sets various conditions with the input device such as keyboards 69. These conditions are memorized in memory 66. When the operator directs the release of the maintenance of these conditions afterwards, the condition memorized in the memory

66 becomes invalid. When CPU60 controls the above-mentioned, first of all, it refers to the condition memorized in memory 66 and obey it when the condition is memorized. When not memorized, it will decide the conditions based on the pre-scanned image data.

**[0121]** The operator can read from the DX code, follow a special order of the customer, and direct the condition setting according to the kind of each film.

**[0122]** Moreover, it is possible to process automatically by setting the condition of each kind of the film beforehand.

**[0123]** Regarding the setting of such a condition, it is also possible that the saturation setting is hold for instance and only the automatically decided condition of the sharpness can be used by making it possible to memorize more detailed condition.

**[0124]** The composition of the image processing device 5 in Fig. 5 was explained above.

**[0125]** Next, the composition of the image processing device 5 to give the image processing to the image data memorized in the 2nd frame memory unit 52 and the 3rd frame memory unit 53 is explained.

**[0126]** The image processing device 5 has the first image processing means 61(Fig. 6) to give image processing of the gradation correction, the color conversion, and the concentration conversion, etc. by the look-up table and the matrix operation to the image data in the 2nd frame memory unit 52 and the 3rd frame memory unit 53, so as to reproduce the color image on color paper in the desired density, gradation, and the tone.

**[0127]** And, it is provided with the second image processing means 62 (Fig. 6) to give image processing of the gradation correction, the color conversion, and the concentration conversion, etc. in the image data memorized in the first frame memory unit 51 by the look-up table and the matrix operation, so as to reproduce on the screen of CRT described later in the desired picture quality. The output of the second frame memory unit 52 and of the third frame memory unit 53 are connected with selector 55.

**[0128]** The image data of the 2nd frame memory unit 52 or the 3rd frame memory unit 53 is selectively input by selector 55 to the first image processing means 61.

**[0129]** Fig. 8 is a block diagram by which details of this first image processing means 61 are shown.

**[0130]** As shown in Fig. 8, the first image processing means 61 provides with the following.

**[0131]** Color concentration gradation conversion means 100 to convert the concentration, color, and gradation of image data, saturation conversion means 101 to convert the saturation data of image data, digital magnification conversion means 102 to convert the number of pixel data, frequency processing means 103 to give the image data frequency processing, and dynamic range conversion means 104 to convert the dynamic range.

**[0132]** These conversion means are usually called pipeline processing. That is, because the processing of the following conversion means are applied at the same time, and immediately after the operation of one conversion means ends, the next conversion starts, the high-speed process is possible.

**[0133]** By the image processing means shown in Fig. 8 not only the gradation correction, the color conversion and the concentration conversion, etc. can be processed but also furthermore, processing by which the sharpness is improved at the same time controlling the granularity can be given. (this technology is applied as the Japanese patent application No.7-337510). Moreover, to the image with large contrast, the automatic cover print which brings an excellent image reproduction can be given (this technology is applied as the Japanese patent application No.7-165965).

**[0134]** Though not related directly to this invention, when the operator inputs the signal to synthesize data, the data signal is output from CPU60 to data synthesis means 75.

**[0135]** Data synthesis means 75 synthesizes the image data which should be synthesized to the obtained image data from synthetic data memory 76. When the instruction signal is not input from keyboard 69 on the other hand, this processing is not executed. Afterwards, the image data is output from data synthesis means 75 to image output device 8.

**[0136]** In this invention, the film is designed so that Dmin is low. In a series of image processing, the zero point adjustment operation which matches Dmin of the film to the base line of a standard characteristic curve is performed.

**[0137]** Moreover, due to the combination of the changes in the concentration magnification of a high spatial frequency element by frequency processing means 103 and the gradation adjustment by gradation processing means 100, the image sharpness is improved by the amendment of the characteristic curve in the toe part and the high density part.

**[0138]** In this case, if the image property obtained under the image processing condition which has already been set is insufficient, the image processing condition is set again.

**[0139]** In addition, by taking the processing to emphasize the fringe of the image and the processing by which the gradation in the low concentration part is raised, the image sharpness can be improved. This is done by frequency processing means 103. That is, the spatial frequency of the image is analyzed. Against the fringe part where the frequency changes greatly and the minute image part where the frequency rises, the emphasizing processing is set.

**[0140]** The accuracy of the correction of the image information has to be only within 10% of the target value in a concentration. Preferably, it is good within 8%. The color balance and the gradation characteristic are judged that the image reproduction can have been done, if the density is within the above-mentioned range.

**[0141]** If the conversion condition of the film is set, you can choose the data conversion condition by reading the kind of the processed film or choose the condition automatically. Moreover, the operator can specify the conversion process-

ing condition of each film. The content of the operation of the image processing device used for the above-mentioned image processing is indicated in Japanese patent application 8-174022 and No.8-182551.

[0142] To the image processing device 5 besides the input bus 63 and out put bus 64 of the 1st frame memory unit 51 and the 2nd frame memory unit 52 and the 3rd frame memory unit 53, the data bus 65 is installed. The following one is connected with data bus 65. CPU60 which controls the entire color image reproduction system, the memory 66 which contains the operation program of CPU60 and the data of image processing condition, the hard disk drive 67 which can preserve image data, CRT68, the keyboard 69, the communication port 70 connected to other color image reproduction systems through telecommunication lines, and the communication line with CPU26 in the transmittance type image device 10.

### 3. Output of picture signal to an output device

[0143] Next, the image output device 8 shown in Fig. 2 and 3 is explained. Though the output of the image information is explained in this invention using the color paper which is a main output object, the object of the output of the image information in this invention is not limited to this. Fig. 9 is a schematic drawing of the image output device 8 for the color image reproduction system which reproduces the color image on color paper based on the image data processed with the image processing device of this invention.

[0144] In Fig. 9, the image output device 8 is provided with the following one. Interface 78 which can be connected to the interface 77 of the image processing device 5 and CPU79 which controls image output device 8, the image data memory 80 which consists of two or more frame memories which memorize the image data from the image processing device 5, D/A converter 81 which converts image data into an analogue signal, the laser-irradiation means 82, the modulator driving means 83 by which modulating signal modulates strength of laser light.

[0145] CPU79 can communicate CPU60 of image processing device 5 via the communication line ( not shown in the figure).

[0146] Fig. 10 is a schematic drawing of laser-irradiation means 82 shown in Fig. 9. The laser-irradiation means 82 is provided with semiconductor laser radiation source 84a, 84b, and 84c. The laser light originated by semiconductor laser radiation source 84b is converted into the green laser light of 532nm in the wave length by wavelength conversion means 85.

[0147] The laser light originated by semiconductor laser radiation source 84c is converted into the blue laser light of 473nm in the wave length by wavelength conversion means 86.

[0148] Red laser light of the arbitrary wave length between 690nm and 670nm, which was originated from semiconductor laser radiation source 84a, is injected in 87R, such as AOM(acoustic optical modulator).

[0149] The green laser light into which the wave length is converted by wavelength conversion means 85 is injected in 87G. And, the blue laser light into which the wave length is converted by wavelength conversion means 86 is an incident in 87B. The modulating signal is input from the modulator driving means 83 to optical modulator 87R, 87G, and 87B respectively, and the strength of the laser light is modulated according to the modulating signal. In this case, if semiconductor laser radiation source 84a can high-speed operate, by modulating this directly the optical modulator 87R can be omitted.

[0150] The laser light whose strength is modulated by the optical modulator 87R, 87G, and 87B can reflect by reflection mirror 88R, 88G, and 88B, and is incident in the polygon mirror 89. Paper is transported, and the scanning line density is 600 an inch, and each pixel is modulated every 100nsec.

[0151] The image output device 8 has magazine 91 by which color paper 90 is stored in the roll state. Color paper 90 is transported in the direction of the sub-scanning along a fixed transportation route. The color paper whose width is from 89mm to 210mm is available. It can be the color paper used in a usual mini lab etc., and you can use a suitable special color paper for high intensity and short time exposure.

[0152] As magazine 91, the one used in a usual mini lab and the one described to the Japanese patent application No.4-317051 for instance are used. In the transportation route of color paper 90, the punching means is provided which can grub the standard hole in the side edge of color paper 90 at every length of frame. The transportation of color paper 90 has synchronized with the drive of other means in image output device 8 according to this standard hole.

[0153] The laser light modulated by optical modulator 87R, 87G, and 87B is scanned to the main scanning direction by polygon mirror 89. Color paper 90 is exposed through lens 93. As for color paper 90, all area are exposed to the laser light because it is transported in the direction of the sub-scanning. The transportation speed of color paper 90 in the direction of the sub-scanning is controlled by CPU79 to synchronize with the rotating speed of a main scanning rate of laser light, that is, the rotating speed of polygon mirror 89.

[0154] Color paper 90 exposed by the laser light is sent to development processing part 94.

[0155] The color development, the blix, and washing are performed. The color image is reproduced in color paper 90 based on image data to which the image is processed with image processing device 5. Color paper 90 to which the color development, the blix treatment, and the washing are performed is sent to dryer part 97. And after drying, based

on the standard hole punched onto the side edge of color paper 90, it is cut in length corresponding to the color image with cutter 98. Then, it is sent to sorter 99. Each number of sheets corresponding to one film F is accumulated. The sorter is separately applied (Japanese patent applications 2-332146th).

[0156] Regarding the color development tank 94, blix tank 95, washing tank 96, dryer part 97, cutter 98, and sorter 99, the ones used in a usual minilab can be used. Though processing method CP47L is adopted in the form of this execution, it is possible to correspond to CP40FA and CP43FA (Processing and the photographic chemicals are both made of the Fuji Photo Film Co., Ltd.).

[0157] In addition, in order to exclude the influence of the characteristic variation of the color paper, the laser radiation source, the modulator, and the development processing machine, and to do the stable image reproduction, the calibration of the image output device can be done. First, using the data memorized, several sets of concentration step patterns of the cyan, magenta, yellow, and gray are exposed. After development, the developed concentration is measured respectively with densitometer automatically. Based on the difference between the concentration which is aimed and measured, the characteristic value given to the modulator to obtain the concentration which should be reproduced is calculated. As a result, reproducing the stable image becomes possible not being influenced by the change of the paper, the device, and the environment etc. The stable image reproduction always becomes possible by controlling such an image output device.

### III. Positive photographic material for output

[0158] As a material for the output to obtain the positive image, as already described, the ink jet, the sublime type heat sensitive transcript material, the color diffusion transfer, the color electrophotography, the heat developing type silver halide color diffusion transfer, the heat developing type multi layer color di-azo material, and the silver halide color photographic material, etc. can be used. If it is a material which can record the picture signal of electricity of a time series, anyone is acceptable.

[0159] The color paper is especially preferable. Some explanation on the color paper will be given.

[0160] In the silver halide color photographic light-sensitive material, which is suitable for this out-put material, various conventionally known photographic elements can be employed.

[0161] For instance, a transmissive type support or reflective type support is used as a support for the photographic material. Among the transmissive type support, a transparent film such as a cellulose triacetate film or a polyethylene terephthalate film, and a polyester film composed of 2,6-naphthalenedicarboxylic acid (NDCA) and ethylene glycol (EG) or composed of NDCA, terephthalic acid and EG having provided thereon an information recording layer such as a magnetic layer are preferably employed. Of the reflective type supports, a laminate composed of plural water-resistant resin layers such as polyethylene layers or polyester layers and containing a white pigment such as titanium oxide in at least one of the resin layers is preferred.

[0162] It is preferred that the water-resistant resin layer contains a fluorescent whitening agent. The fluorescent whitening agent may also be dispersed in a hydrophilic colloid layer of the photographic light-sensitive material. Preferred fluorescent whitening agents used include benzoxazole series, cumarin series and pyrazoline series compounds. Fluorescent whitening agents of benzoxazolyl naphthalene series and benzoxazolyl stilbene series are more preferably used. The amount of the fluorescent whitening agent to be used is not particularly limited and preferably in a range of from 1 to 100 Mg/m<sup>2</sup>. A mixing ratio of the fluorescent whitening agent to be used in the water-resistant resin layer is preferably from 0.0005 to 3% by weight, and more preferably from 0.001 to 0.5% by weight of the resin.

[0163] Further, a transmissive type support and a reflective type support each having provided thereon a hydrophilic colloid layer containing a white pigment may be employed.

[0164] Moreover, a support having a mirror plate reflective metal surface or a secondary diffusion reflective metal surface may be used as the reflective type support.

[0165] A silver chloride or silver chlorobromide emulsion having a silver chloride content of 95 mol% or more is preferably employed as the silver halide emulsion in the color photographic light-sensitive material in view of rapid processing suitability. Further, a silver halide emulsion having a silver chloride content of 98 mol% or more is more preferred. Of these silver halide emulsions, those having a silver bromide localized phase on the surface of silver chloride grain is particularly preferred, since high sensitivity as well as stabilization of photographic characteristics are achieved.

[0166] With respect to the reflective type support, silver halide emulsion, heterogeneous metal ion doped in silver halide grain, stabilizer and anti-foggant for silver halide emulsion, chemical sensitization (chemical sensitizer), spectral sensitization (spectral sensitizer), cyan coupler, magenta coupler, yellow coupler, emulsified dispersion method of coupler, color image stabilizer (anti-staining agent), color fading preventing agent, dye (colored layer), gelatin, layer construction of photographic material and pH of coated layer, those described in the patents shown in Table 1 and Table 2 below are preferably used in the present invention.

TABLE 1

	Photographic Element	JP-A-7-104448	JP-A-7-77775	JP-A-7-310895
5	Reflective Type Support	Col. 7, line 12 to Col. 12, line 19	Col. 35, line 43 to Col. 44, line 1	Col. 5, line 40 to Col. 9, line 26
	Silver Halide Emulsion	Col. 72, line 29 to Col. 74, line 18	Col. 44, line 36 to Col. 46, line 29	Col. 77, line 48 to Col. 80, line 28
10	Heterogeneous Metal Ion	Col. 74, lines 19 to 44	Col. 46, line 30 to Col. 47, line 5	Col. 18, line 29 to Col. 81, line 26
15	Stabilizer and Anti-foggant	Col. 75, lines 9 to 18	Col. 47, lines 20 to 29	Col. 18, line 11 to Col. 31, line 37 (particularly, mercapto heterocyclic compound)
20	Chemical Sensitization (Chemical Sensitizer)	Col. 74, line 45 to Col. 75, line 6	Col. 47, lines 7 to 17	Col. 81, lines 9 to 17
	Spectral Sensitization (Spectral Sensitizer)	Col. 75, line 19 to Col. 76, line 45	Col. 47, line 30 to Col. 49, line 6	Col. 81, line 21 to Col. 82, line 48
25	Cyan Coupler	Col. 12, line 20 to Col. 39, line 49	Col. 62, line 50 to Col. 63, line 16	Col. 88, line 49 to Col. 89, line 16
30	Yellow Coupler	Col. 87, line 40 to Col. 88, line 3	Col. 63, lines 17 to 30	Col. 89, lines 17 to 30

TABLE 2

	Photographic Element	JP-A-7-104448	JP-A-7-77775	JP-A-7-310895
35	Magenta Coupler	Col. 88, line 4 to 18	Col. 63, line 31 to Col. 64, line 11	Col. 32, line 34 to Col. 77, line 44 and col. 89, lines 32 to 46
40	Emulsified Dispersion Method of Coupler	Col. 71, line 3 to Col. 72, line 11	Col. 61, lines 36 to 49	Col. 87, line 35 to 48
45	Color Image Stabilizer (Anti-staining Agent)	Col. 39, line 50 to Col. 70, line 9	Col. 651, line 50 to Col. 62, line 49	Col. 87, line 49 to Col. 88, line 48
	Color Fading Preventing Agent	Col. 70, line 10 to Col. 71, line 2		
50	Dye (Colored Layer)	Col. 77, line 42 to Col. 78, line 41	Col. 7, line 14 to Col. 19, line 42 and Col. 50, line 3 to Col. 51, line 14	Col. 9, line 27 to Col. 18, line 10
55	Gelatin	Col. 78, lines 42 to 48	Col. 51, lines 15 to 20	Col. 83, lines 13 to 19
	Layer Construction of Photographic Material	Col. 39, lines 11 to 26	Col. 44, lines 2 to 35	Col. 31, lines 38 to Col. 32, line 33

TABLE 2 (continued)

Photographic Element	JP-A-7-104448	JP-A-7-77775	JP-A-7-310895
pH of Coated Layer	Col. 72, lines 12 to 18		
Scanning Exposure	Col. 76, line 6 to Col. 77, line 41	Col. 49, line 7 to Col. 50, line 2	Col. 82, line 49 to Col. 83, line 12
Preservative in Developing Solution	Col. 88, line 19 to Col. 89, line 22		

**[0167]** The cyan couplers, magenta couplers and yellow couplers which can be suitably employed in this material also include those described in JP-A-62-215272, page 91 right upper column, line 4 to page 121, left upper column, line 6, JP-A-2-33144, page 3, right upper column, line 14 to page 18, left upper column, last line and page 30, right upper column, line 6 to page 35, right lower column, line 11, and EP-A-355660, page 4, lines 15 to 27, page 5, line 30 to page 28, last line, page 45, lines 29 to 31 and page 47, line 23 to page 63, line 50.

**[0168]** The bactericides and anti-mold agents described in JP-A-63-271247 are suitably used in the present invention.

**[0169]** Gelatin is preferably employed as a hydrophilic colloid in a photographic layer constituting the photographic light-sensitive material. An amount of heavy metal, for example, iron, copper, zinc or manganese, which is included as an impurity in gelatine, is preferably not more than 5 ppm, more preferably not more than 3 ppm.

**[0170]** This photographic light-sensitive material is used in digital scanning exposure system using monochromatic high density light, such as a gas laser, a light emitting diode, a semiconductor laser, a second harmonic generation light source (SHG) comprising a combination of non-linear optical crystal with a semiconductor laser or a solid state laser using a semiconductor laser as an excitation light source. For obtaining a compact and inexpensive system, it is preferred to use a semiconductor laser, or a second harmonic generation light source (SHG) comprising a combination of non-linear optical crystal with a semiconductor laser or a solid state laser. In particular, for designing a compact and inexpensive apparatus having a longer duration of life and high stability, it is preferred to use a semiconductor laser, and at least one of exposure light sources should be a semiconductor laser.

**[0171]** When such a scanning exposure light source is used, the spectral sensitivity maximum of the photographic light-sensitive material for the out-put material of this invention can be appropriately set according to the wavelength of the scanning exposure light source to be used. As an oscillation wavelength of a laser can be made half using an SHG light source comprising a combination of non-linear optical crystal with a solid state laser using a semiconductor laser as an excitation light source or a semiconductor laser, blue light and green light can be obtained. Accordingly, it is possible to have the spectral sensitivity maximum of the photographic light-sensitive material in normal three regions of blue, green and red.

**[0172]** The exposure time in the scanning exposure is defined as the time necessary to expose the pixel size with the pixel density being 400 dpi, and preferred-exposure time is 10-4 second or less and more preferably 10-6 second or less.

#### IV. Color negative film

**[0173]** About the color negative film used for this invention. Because the method of achieving the decrease of  $D_{min}$  has already been described, a supplementary explanation of the color negative film used for this inventions is done.

**[0174]** The color negative film of this invention is a type to which the gradation and  $D_{min}$  are changed from the general color negative film provided from each maker. And, the one with the reduced inter color effect is preferable.

**[0175]** A typical example of the light-sensitive materials of the present invention is a silver halide photographic light-sensitive material having, on the support, at least one light-sensitive layer constituted by a plurality of silver halide emulsion layers which are sensitive to the same color but which have different sensitivities or speeds. The light-sensitive layer is a unit light-sensitive layer which is sensitive to any one of blue light, green light and red light and, in a multi-layered silver halide color photographic light-sensitive material, a generally adopted order of the unit light-sensitive layers from the support is red-sensitive layer, a green-sensitive layer and a blue-sensitive layer. However, according to the intended use, this order of layers may be reversed, or a layer having a different color sensitivity may be sandwiched between layers having the same color sensitivity in accordance with the application. Non-light-sensitive layers can be formed between the silver halide light-sensitive layers and as the uppermost layer and the lowermost layer. These non-light-sensitive layers can contain, e.g., couplers, DIR compounds, color mixture preventives described later. As a plurality of silver halide emulsion layers constituting a unit light-sensitive layer, a two-layered structure of high-

speed and low-speed emulsion layers can be preferably arranged such that the sensitivity or speed is sequentially decreased toward a support as described in West German Patent 1,121,470 or British Patent 923,045. Alternatively, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541 and JP-A-62-206543, layers may be arranged such that a low-speed emulsion layer is formed remotely from a support and a high-speed layer is formed close to the support.

**[0176]** Specifically, layers may be arranged from the remotest side from a support in an order of low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)/low-speed green-sensitive layer (GL)/high-sensitive red-sensitive layer (RH)/low-speed red-sensitive layer (RL), or BH/BL/GL/GH/RH/RL, or BH/BL/GH/GL/RL/RH.

**[0177]** Further, layers may be arranged from the remotest side from a support in an order of blue-sensitive layer/GH/RH/GH/RL as described in JP-B-55-34932. Alternatively, layers may be arranged of from the remotest side from a support in an order of blue-sensitive layer/GL/RL/GH/RH as described in JP-A-56-25738 and JP-A-62-63936.

**[0178]** Further, as described in JP-B-15495, three layers may be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an intermediate layer, and a silver halide emulsion layer having sensitivity lower than that of the intermediate layer is arranged as a lower layer, i.e., the three layers having different sensitivities may be arranged such that the sensitivity is sequentially decreased toward the support. Also, when the light-sensitive material comprises the three layers having different sensitivities or speed, these layers may be arranged from far to near the support in the order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer within a layer sensitive to one and the same color sensitivity as described in JP-A-59-202464.

**[0179]** In addition, an order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer, or an order of low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer may be adopted.

**[0180]** Furthermore, the arrangement can be changed as described above, even when four or more layers are formed.

**[0181]** In order to improve color reproductivity, a donor layer (CL) having different spectral sensitivity distribution from that of a main light-sensitive layer such as BL, GL and RL and having interlayer effect, described in the specification of U.S. Patent 4,663,271, U.S. Patent 4,705,744, U.S. Patent 4,707,436, JP-A-62-160448 and JP-A-63-89850, is preferably arranged adjacent to or in the vicinity of the main light-sensitive layer.

**[0182]** A preferable silver halide to be used in photographic emulsion layers of the photographic light-sensitive material of the present invention is silver iodobromide, silver iodochloride or silver iodochlorobromide containing about 30 mol% or less of silver iodide. A particularly preferable silver halide is silver iodobromide or silver iodochlorobromide each containing about 2 mol% to about 10 mol% of silver iodide.

**[0183]** The silver halide grains contained in the photographic emulsion may be in the form of regular crystals, such as cubes, octahedrons and decahedrons, irregular crystals, such as spheres and tabulars, crystals having defects such as twin planes, or composite shapes thereof.

**[0184]** The grain sizes of the silver halide may range from fine grains having a grain diameter of about 0.2  $\mu\text{m}$  or less or to large grains having a diameter of the projected area of a grain of up to about 10  $\mu\text{m}$ . Further, the silver halide emulsion may be a polydisperse emulsion or a monodisperse emulsion.

**[0185]** The silver halide photographic emulsion usable in the present invention can be prepared by the methods described, for example, in Research Disclosure (hereinafter abbreviated to RD) No. 17643 (December 1978), pages 22-23, "I. Emulsion Preparation and Types"; RD No. 18716 (November 1979), page 648, and RD No. 307105 (November 1989), pages 863-865; P. Glafkides, "Chimie et Physique Photographiques", 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.

**[0186]** Also preferable is the monodisperse emulsion described in U.S. Patent 3,574,628, U.S. Patent 3,655,394 and British Patent 1,413,748.

**[0187]** Further, tabular grains having an aspect ratio of about 3 or more can also be used in the present invention. The tabular grains can be easily prepared by the methods described in Gutoff, "Photographic Science and Engineering", Vol. 14, pp. 248-257 (1970); U.S. Patents 4,434,226; 4,414,310; 4,433,048 and 4,439,520, and British Patent 2,112,157.

**[0188]** The crystal structure may be uniform, may have different halogen compositions in its interior and exterior, or may be layered structure. Alternatively, silver halide having different compositions may be joined by an epitaxial junction, or a compound other than a silver halide such as silver rhodanide or lead oxide may be joined. A mixture composed of grains having various crystal forms may also be used.

**[0189]** The above-mentioned emulsion needs to be a negative-type emulsion, although it may be of a surface latent image type which forms a latent image mainly on the surface of the grains, an inner latent image type which forms a latent image inside the grains, or other type which forms a latent image both inside and outside the grain. The emulsion belonging to the inner latent image type may be of the inner latent image type having a core/shell structure described in JP-A-63-264740, the method for making which emulsion is described in JP-A-59-133542. The thickness of the shell

for this emulsion is preferably 3 to 40 nm and most preferably 5 to 20 nm, although the thickness varies depending on processing conditions for development and the like.

**[0190]** Prior to the use of the light-sensitive material of present invention, the silver halide usually undergoes a chemical ripening, a physical ripening, and a spectral sensitization steps. The additives which are used at such steps are described in RD No. 17643, RD No. 18716 and RD No. 307105 and are summarized later in a table with the indications of the relevant places of description.

**[0191]** In the light-sensitive material of the present invention, a mixture of two or more emulsions, which differ from one another in at least one of the characteristics selected from the group consisting of grain size, grain size distribution, halogen composition, shape of grain and sensitivity, can be used in the same layer.

**[0192]** It is preferable to use non-light-sensitive silver halide fine grains, in the present invention. The non-light-sensitive silver halide fine grains mean the silver halide fine grains which are not sensitized in the imagewise exposure for forming a dye image and are substantially undeveloped when processed for development. Preferably, the non-light-sensitive silver halide fine grains are not fogged in advance. The fine-grain silver halide has a silver bromide content of 0 to 100 mol%. If necessary, the fine-grain silver halide may further contain silver chloride and/or silver iodide. Preferred silver iodide content is 0.5 to 10 mol%. The average grain diameter (average value of the equivalent-circle diameter of projected area) of the fine-grain silver halide is preferably 0.01 to 0.5  $\mu\text{m}$ , and more preferably 0.02 to 0.2  $\mu\text{m}$ . The fine-grain silver halide can be prepared by the same method as that for a conventional light-sensitive silver halide. No optical sensitization or spectral sensitization is necessary for the surface of the grains of the silver halide. However, it is preferable to add to the silver halide grains a known stabilizer such as a triazole compound, an azaindene compound, a benzothiazole compound, a mercapto compound or a zinc compound, before the silver halide is added to a coating solution. A layer, which contains the fine-grain silver halide, may further contain colloidal silver.

**[0193]** The photographic additives usable in the present invention are also described in RD and the following table shows the additives together with the relevant places of description.

TABLE 3

Additives	RD17643	RD18716	RD307105
1. Chemical sensitizer	p23	p648,r.c.	p866
2. Sensitivity increasing agent		p648,r.c.	
3. Spectral sensitizer Super sensitizer	p23-24	p648,r.c.-p649,r.c.	p866-868
4. Brightener	p24	p647,r.c.	p868
5. Light absorber Filter dye, Ultraviolet absorbent	p25-26	p649,r.c.-p650,1.c.	p873
6. Binder	p26	p651,1.c.	p873-874
7. Plasticizer, Lubricant	p27	p650,r.c.	p876
B. Coating aid, Surfactant	p26-27	p650,r.c.	p875-876
9. Antistatic agent	p27	p650,r.c.	p876-877
10. Matting agent			p878-879
(Note)			
p: page			
right column			
l.c.: left column			

**[0194]** Various dye formation couplers can be used in the light-sensitive material of the present invention, and the following couplers are particularly preferable.

**[0195]** Yellow couplers: couplers represented by Formulas (I) and (II) in European Patent (hereinafter referred to as EP 502,424A; couplers (particularly Y-28 on page 18) represented by Formulas (1) and (2) in EP 513,496A; a coupler represented by Formula (I) in claim 1 of EP 568,037A; a coupler represented by Formula (I) in claim 1, lines 45 to 55,



in U.S. Patent 5,066,576; a coupler represented by Formula (I) in paragraph 0008 of JP-A-4-274425; couplers (particularly D-35 on page 18) described in claim 1 on page 40 in EP 498,381A1; couplers (particularly Y-1 (page 17) and Y-54 (page 41)) represented by Formula (Y) on page 4 in EP 447,969A1; and couplers (particularly II-17 and II-19 (column 17) and II-24 (column 19)) represented by Formulas (II) to (IV) in column 7, lines 36-58, in U.S. Patent 4,476,219.

**[0196]** Magenta couplers: JP-A-3-39737 (L-57 (page 11, lower right column), L-68 (page 12, lower right column), and L-77 (page 13, lower right column); (A-4)-63 (page 134), and (A-4)-73 and (A-4)-75 (page 139) in EP 456,257; M-4 and M-6 (page 26), and M-7 (page 27) in EP 486,965; M-45 (page 19) in EP 571,959A; (M-1) (page 6) in JP-A 5-204196; and M-22 in paragraph 0237 of JP-A-4-362631.

**[0197]** Cyan couplers: CX-1, CX-3, Ck-4, CX-5, CX-11, CX-12, CX-14, and CX-15 (pages 14 to 16) in JP-A-4-204843; C-7 and C-10 (page 35), C-34 and C-35 (page 37), and (I-1) and (I-17) (pages 42 and 43) in JP-A-4-43345; and couplers represented by Formula (Ia) and (Ib) described in claim 1 of JP-A-6-67385.

**[0198]** Polymer couplers: P-1 and P-5 (page-11) in JP-A-2-44345.

**[0199]** Couplers for forming a colored dye having a proper diffusibility are preferably those described in U.S. Patent 4,366,237, British Patent 2,125,570, EP 96,873B and West German Laid-open Patent Application 3,234,533.

**[0200]** Couplers for correcting unnecessary absorption of a colored dye are yellow colored cyan couplers (particularly YC-86 on page 84) represented by Formulas (CI), (CII), (CIII) and (CIV) described on page 5 in EP 456,257A1; yellow colored magenta couplers ExM-7 (page 202), Ex-1 (page 249) and Ex-7 (page 251) in EP 456,257A; magenta colored cyan couplers CC-9 (column 8) and CC-13 (column 10) described in U.S. Patent 4,833,009; (2) (column 8) in U.S. Patent 4,838,136; and colorless masking couplers (particularly compound examples on pages 36 to 45) represented by Formula (A) described in claim 1 of WO 92/11,575. But these colored couplers are not preferably used in this invention as mentioned before.

**[0201]** Example of a compound (including a coupler) which reacts with a developing agent oxidized form and releases a photographically useful compound residue are as follows. Development inhibitor release compounds: compounds (particularly T-101 (page 30), T-104 (page 31), T-113 (page 36), T-131 (page 45), T-144 (page 51) and T-158 (page 58)) represented by Formulas (I), (II), (III) and (IV) described on page 11 in EP 378,236A; compounds (particularly D-49 (page 51)) represented by Formula (I) described on page 7 in EP 436,938A2; compounds (particularly (23) (page 11)) represented by Formula (I) in EP 568,037A; compound (particularly I-(1) on page 29) represented by Formulas (I), (II) and (III) described on pages 5 and 6 in EP 440,195A2; (But these compounds are not preferably used in this invention as mentioned before.) bleaching accelerator release compounds: compound (particularly (60) and (61) on page 61) represented by Formulas (I) and (I') described on page 5 in EP 310,125A2; and compounds (particularly (7) (page 7)) represented by Formula (I) described in claim 1 of JP-A-6-59411; ligand release compounds: compound (particularly compounds in column 12, lines 21 to 41) represented by LIG-X described in claim 1 of U.S. Patent 4,555,478; leuco dye release compounds; compounds 1 to 6 in columns 3 to 8 of U.S. Patent 4,749,641; fluorescent dye release compounds; compounds (particularly compounds 1 to 11 in columns 7 to 10) represented by COUP-DYE described in claim 1 of U.S. Patent 4,774,181; development accelerators of fogging agent release compounds; compounds (particularly compound (I-22) in column 25) represented by Formulas (1), (2) and (3) described in column 3 of U.S. Patent 4,656,123, and compounds represented by ExZK-2 described on page 75, lines 36 to 38, in EP 450,637A2; and compounds which release a group which does not function as a dye unless it splits off; compounds (particularly Y-1 to Y-19 in columns 25 to 36) represented by Formula (I) in claim 1 of U.S. Patent 4,857,447.

**[0202]** Preferable examples of additive other than couplers are as follows:

**[0203]** Dispersants of an oil-soluble organic compound: P-3, P-5, P-16, P-19, P-25, P-30, P-42, P-49, P-54, P-55, P-66, P-81, P-85 and P-93 (pages 140 to 144) in JP-A-62215272; impregnating latexes of an oil-soluble organic compound: latexes described in U.S. Patent 4,199,363; developing agent oxidized form scavengers: compounds (particularly I-(1), I-(2), I-(6) and I-(12) (columns 4 and 5)) represented by Formula (I) in column 2, lines 54 to 62, in U.S. Patent 4,978,606, and formulas (particularly compound 1 (column 3)) in column 2, lines 5 to 10, in U.S. Patent 4,923,787; stain inhibitors: Formulas (I) to (III) on page 4, lines 30 to 33, particularly I-47, I-72, III-1 and III-27 (pages 24 to 48) in EP 298,321A; brown inhibitors: A-6, A-7, A-20, A-21, A-23, A-24, A-25, A-26, A-30, A-37, A-40, A-42, A-48, A-63, A-90, A-92, A-94 and A-164 (pages 69 to 118) in EP 298,321A, II-1 to III-23, particularly III-10, in columns 25 to 38 of U.S. Patent 5 122,444, I-1 to III-4, particularly II-2, on pages 8 to 12 in EP 471,347A, and A-1 to A-48, particularly A-39 and A-42, in columns 32 to 40 of U.S. Patent 5,139,931; materials which reduce the use amount of a color enhancer or a color amalgamation inhibitor: I-I to II-15, particularly I-46, on pages 5 to 24 in EP 411,324A; formalin scavengers: SCV-1 to SCV-8, particularly SCV-8, on pages 24 to 29 in EP 477,932A; film hardeners: H-1, H-4, H-6, H-8 and H-14 on page 17 in JP-A-1-214845, compounds (H-1 to H-54) represented by Formulas (VII) to (XII) in columns 13 to 23 of U.S. Patent 4,618,573, compounds (H-1 to H-76), particularly H-14, represented by Formula (6) on page 8, lower right column, in JP-A-2-214852, and compounds described in claim 1 of U.S. Patent 3,325,287; development inhibitor precursors: P-24, P-37 and P-39 (pages 6 and 7) in J-A-62-168139 and compounds described in claim 1, particularly 28 and 29, in column 7, of U.S. Patent 5,019,492; antiseptic agents and mildewproofing agents:

I-1 to III-43, particularly II-1, II-9, II-10, II-18 and III-25, in columns 3 to 15 of U.S. Patent 4,923,790; stabilizers and  
 aitifoggants: I-1 to (14), particularly I-1, 60, (2) and (13), in columns 6 to 16 of U.S. Patent 4,923,793, and compounds  
 1 to 65, particularly compound 36, in columns 25 to 32 of U.S. Patent 4,952,483; triphenylphosphine selenide: com-  
 5 pound 50 described in JP-A-5-40324; dyes: a-1 to b-20, particularly a-1, a-12, a-18, a-27, a-35 and 3-26 and b-5 on  
 pages 15 to 18, and V-1 to V-23, particularly V-1, on pages 27 to 29 in JP-A-3-156450, F-I-1 to F-II-43, particularly F-  
 I-11 and F-11-8, on pages 33 to 55 in EP 445,727A, III-1 to III-36, particularly III-1 and III-3, on pages 17 to 28 in EP  
 457,153A, fine crystal dispersions of Dye-1 to Dye-124 on pages 8 to 26 in WO 88/04,794, compounds 1 to 22, par-  
 10 ticularly compound 1, on pages 6 to 11 in EP 319,999A, compounds D-1 to D-87 (pages 3 to 28) represented by  
 Formulas (1) to (3) in EP 519,306A, compounds 1 to 22 (columns 3 to 10) represented by Formulas (I) in U.S. Patent  
 4,268,622, and compounds (1) to (31) (columns 2 to 9) represented by Formulas (I) in U.S. Patent 4,923,788; and UV  
 absorbents: compounds (18b) to (18r) and 101 to 427 (pages 6 to 9) represented by Formulas (1) in JP-A-46-3335,  
 compounds (3) to (66) (pages 10 to 44) represented by Formula (I) and compounds HBT-1 to HBT-10 (page 14) rep-  
 15 resented by Formula (III) in EP 520,938A, and compounds (1) to (31) (columns 2 to 9) represented by Formula (1) in  
 EP 521,823A.

**[0204]** The present invention can be applied to various color light-sensitive materials. The present invention is also  
 suited to film units with lens described in JU-B-2-32615 and JU-B-3-38784 ("JU-B" means Published Examined Jap-  
 anese Utility Model Application).

**[0205]** A support which can be suitably used in the present invention is described in, e.g., RD No. 17643, page 28,  
 RD No. 18716, from right column, page 647, to left column, page 648, and RD No. 307105, page 879.

**[0206]** Typical of useful polymeric film supports are films of cellulose nitrate and cellulose esters, such as cellulose  
 20 triacetate, and diacetate, polystyrene, polyamides, homo- and copolymers of vinyl chloride, poly (vinyl acetale), poly-  
 carbonate, homo- and copolymers of olefins, such as polyethylene and polypropylene, and polyesters of dibasic aro-  
 matic carboxylic acids with divalent alcohols, such as polyethylene therephtalate.

**[0207]** In the light-sensitive material of the present invention, the sum total of film thickness of all hydrophilic colloid  
 25 layers on the side having the emulsion layers is preferably 22  $\mu\text{m}$  or less, more preferably 18  $\mu\text{m}$  or less, particularly  
 preferably 18  $\mu\text{m}$  or less. A film swell speed  $T_{1/2}$  is preferably 30 seconds or less, and more preferably 20 seconds or  
 less.  $T_{1/2}$  is defined as a time which the film thickness requires to reach 1/2 of a saturation film thickness which is 90%  
 of a maximum swell film thickness reached when processing is performed by using a color developer at 300C for 3  
 30 min and 15 seconds. The film thickness means the thickness of a film measured under moisture conditioning at a  
 temperature of 250°C and a 55% relative humidity (two days).  $T_{1/2}$  can be measured by using a swell meter described  
 in Photographic Science Engineering, A. Green et al., Vol. 19, No. 2, pp. 124-129.  $T_{1/2}$  can be adjusted by adding film  
 hardening agent to gelatine as a binder or changing ageing conditions after coating. The swell ratio is preferably 150  
 to 400%. The swell ratio can be calculated from the maximum swell film thickness under the conditionings mentioned  
 above by using (maximum swell film thickness-film thickness) / film thickness.

**[0208]** In the light-sensitive material of the present invention, hydrophilic colloid layers (called back layers) having a  
 35 total dried film thickness of 2 to 20  $\mu\text{m}$  are preferably formed on the side opposite to the side having emulsion layers.  
 The back layers preferably contain, e.g., the light absorbent, the filter dye, the ultraviolet absorbent, the antistatic agent,  
 the film hardener, the binder, the plasticizer, the lubricant, the coating aid, and the surfactant, described above. The  
 swell ratio of the back layer is preferably 150 to 500%.

**[0209]** The light-sensitive material of the present invention can be processed for development by a conventional  
 40 method described in aforesaid RD No. 17643, pages 28 and 29, RD No. 18716, page 651, from left column to right  
 column, and RD No. 307105, pages 880 and 881.

**[0210]** The processing solution for a color negative film of the present invention is described below.

**[0211]** The color developing solution of the present invention may contain the compounds described in JP-A-  
 45 4-121739, page 9, upper right column, line 1 to page 11, lower left column, line 4. Preferred developing agents for the  
 rapid processing are 2methyl-4-(N-ethyl-N-(2-hydroxyethyl)amino)aniline, 2methyl-4-(N-ethyl-N-(3-hydroxypropyl)  
 amino)aniline and 2-methyl-4-(N-ethyl-N-(4-hydroxybutyl)amino)aniline.

**[0212]** The concentration of these color developing agents is preferably 0.01 to 0.08 mol, more preferably 0.015 to  
 0.06 mol, and most preferably 0.02 to 0.05 mol per liter of the color developing solution. The concentration of these  
 50 color developing agents in a replenisher solution of the color developing solution is preferably 1.1 to 3 times, more  
 preferably 1.3 to 2.5 times, the concentration in the color developing solution.

**[0213]** The color developing solution of the present invention may contain a hydroxylamine as a general purpose  
 preservative. If a higher-level preservation is required, preferable preservatives are hydroxylamine derivatives having  
 substituents such as alkyl, hydroxyalkyl, sulfoalkyl and carboxyl groups, preferred examples of which are N,N-di(sul-  
 55 foethyl)hydroxylamine, monomethylhydroxylamine, dimethylhydroxylamine, monoethylhydroxylamine, diethylhydroxy-  
 lamine and N,N-di(carboxylethyl)hydroxylamine. Among the above-mentioned derivatives, N,N-di(sulfoethylhydroxy-  
 lamine is particularly preferable. Although any of these derivatives may be used in combination with hydroxylamine,  
 preferably one, or two or more of these derivatives are used instead of hydroxylamine.

**[0214]** The concentration of the preservative is preferably 0.02 to 0.2 mol, more preferably 0.03 to 0.15 mol, and most preferably 0.04 to 0.1 mol per liter of the color developing solution. The concentration of the preservative in a replenisher solution of the color developing solution is 1.1 to 3 times the concentration in the mother solution (i.e., the solution in the processing tank).

**[0215]** In order to prevent the tarring of the developing agent oxidized form, the color developing solution contains a sulfite. The concentration of the sulfite is preferably 0.01 to 0.05 mol and particularly preferably 0.02 to 0.04 mol per liter of the color developing solution. The concentration of the sulfite in a replenisher solution of the color developing solution is 1.1 to 3 times the concentration mentioned above.

**[0216]** The pH value of the color developing solution is preferably 9.8 to 11.0 and particularly preferably 10.0 to 10.5. The pH value of a replenisher solution of the color developing solution is set to a value preferably 0.1 to 1.0 above the above-mentioned values. In order to maintain pH at the above-mentioned values in a stable manner, a known buffer solution such as a carbonate, a phosphate, a sulfosalicylate or a borate is used.

**[0217]** The quantity of replenisher of the color developing solution is preferably 80 to 1,300 mL per m<sup>2</sup> of the light-sensitive material. From the viewpoint of reducing the polluting load to environment, the quantity should be reduced and is preferably 80 to 600 mL, more preferably 80 to 400 mL.

**[0218]** The bromide ion concentration in the color developing solution is usually 0.01 to 0.06 mol per liter of the color developing solution. Preferably, the bromide ion concentration is set to 0.015 to 0.03 mol per liter of the color developing solution for the purpose of fog inhibition and enhancement of discrimination while maintaining the sensitivity and for overcoming the problem of graininess. If the bromide ion concentration is set to the above-mentioned range, the replenisher solution needs to contain the bromide ions at the concentration given by the following equation; provided that the replenisher solution preferably contains no bromide ion if the calculated value C is negative.

$C = A - W/V$  where

C: Bromide ion concentration (mol/L) of the replenisher solution of the color developing solution;

A: target bromide ion concentration (mol/L) in the color developing solution;;

W: Amount (mol) of the bromide ions which dissolve into the color developing solution from the light-sensitive material when 1 m<sup>2</sup> of the light-sensitive material was processed for development; and

V: Quantity of replenisher of the color developing solution per m<sup>2</sup> of the light-sensitive material.

**[0219]** If the quantity of replenisher is reduced or the bromide ion concentration is set to a large value, it is preferable to use development accelerators, such as pyrazolidones represented by l-phenyl-3-pyrazolidone or 1-phenyl-2-methyl-2-hydroxymethyl-3-pyrazolidone, and thioether compounds represented by 3,6-dithia-1,8-octanediol, as a means for increasing the sensitivity.

**[0220]** The compounds or processing conditions, which are described in JP-A-4-125558, page 4, lower left column, line 15 to page 7, lower left column, line 6, can be applied to the processing solution having a bleaching power of the present invention.

**[0221]** A preferable bleaching agent has a redox potential of 150 mV or more. Preferred examples of the bleaching agents are described in JP-A-5-72694 and JP-A-5-173312. Particularly preferred examples are 1,3-diaminopropane-tetraacetic acid and ferric complex salts of the compounds shown as example 1 in JP-A-5-173312.

**[0222]** It is preferable to use the ferric complex salts of the compounds described in JP-A-4-251845, JP-A-268552, EP 588,289, EP 591-, 934 and JP-A-6-208213 as a bleaching agent to increase the biodegradability of the bleaching agent. The concentration of the bleaching agent is preferably 0.05 to 0.3 mol per liter of the solution having a bleaching power. Preferably, the concentration is set to 0.1 to 0.15 mol in order to reduce the discharge amount to environments. If the solution having a bleaching power is a bleaching solution, it is desirable that the solution contain the bromide ions at a concentration of 0.2 to 1 mol, preferably 0.3 to 0.8 mol, per liter of the solution.

**[0223]** The replenisher solution of the solution having a bleaching power needs to have concentration of the components shown below which are basically calculated by the following equation. As a result, the concentration in the mother solution can be maintained at a constant value.

$$C_R = C_T \times (V_1 + V_2)/V_1 + C_p$$

where

$C_R$ : Concentration of the component in the replenisher solution;

$C_T$ : Concentration of the compound in the mother solution (solution in the processing tank) ;

$C_p$ : Concentration of the component consumed during the processing;

$V_1$ : Quantity (mL) of replenisher solution having a bleaching power per m<sup>2</sup> of the light-sensitive material; and

$V_2$ : Quantity (mL) carried over from the preceding bath per  $m^2$  of the light-sensitive material.

**[0224]** Further, it is preferable that the bleaching solution contain a pH buffering agent, preferred examples of which are low-odor dicarboxylic acids such as succinic acid, maleic acid, malonic acid, glutaric acid and adipic acid. It is also preferable to use known bleaching accelerators described in JP-A-53-95630, RD No. 17129 and U.S. Patent 3,893,858.

**[0225]** It is desirable that the bleaching solution be supplied with 50 to 1,000 mL, preferably 80 to 500 mL, and most preferably 100 to 300 mL of a replenisher solution of the bleaching solution per  $m^2$  of the light-sensitive material. Further, it is preferable that the bleaching solution be aerated.

**[0226]** The compounds or processing conditions, which are described in JP-A-4-125558, page 1, lower left column, line 10 to page 8, lower right column, line 19, can be applied to the processing solution having a fixing power of the present invention.

**[0227]** In particular, in order to increase the fixing speed and the preservability of the solution, the solution having a fixing power preferably contains the compounds represented by the Formulas (I) and (II) in JP-A-6-301169 singly or as a combination. In addition-, from the viewpoint of the enhancement of the preservability, it is preferable to use a sulfinic acid, such as p-toluenesulfinic acid salt, described in JP-A-1-224762.

**[0228]** When viewed from the enhancement of the desilvering capability, it is desirable that the solution having a bleaching power or a fixing power contain ammonium as a cation. However, it is preferable to decrease the ammonium content of the solution or to make the solution ammonium-free from the viewpoint of the reduction of the environmental pollution.

**[0229]** It is particularly preferable to carry out the jet-agitation of the solution described in JP-A-1-309059 at the steps of bleaching, bleach-fixing and fixing.

**[0230]** The quantity of replenisher at a bleach-fixing step or fixing step is 100 to 1,000 mL, preferably 150 to 700 mL, and most preferably 200 to 600 mL per  $m^2$  of the light-sensitive material.

**[0231]** Preferably, the bleach-fixing step or fixing step is provided with an in-line or off-line silver recovery unit so that the silver is recovered. If an in-line unit is used, the quantity of replenisher can be reduced, because the silver concentration in the solution in the bath becomes smaller owing to the treatment, meanwhile, it is also desirable to remove the silver by means of an off-line unit so that the residual solution is re-used as a replenisher solution.

**[0232]** The bleach-fixing step or fixing step may comprises a plurality of processing tanks, which are preferably arranged by a multistage counter-current method employing cascade piping. Because of the balance with the size of the processor, in general a two-tank cascade structure is efficient wherein the ratio of the processing time between the fore tank and the rear tank is preferably in the range of 0.5:1 to 1:0.5 and particularly preferably in the range of 0.8:1 to 1:0.8.

**[0233]** From the viewpoint of increasing the preservability, the bleach-fixing solution or fixing solution preferably contains a free chelating agent which is not in the form of a complex with a metal. These chelating agents are preferably biodegradable chelating agents previously described in connection with the bleaching solution.

**[0234]** The techniques described in JP-A-4-125558, page 12, lower right column, line 6 to page 13, lower right column, line 16 can be preferably applied to the water-washing and stabilizing step. Particularly, in order to preserve the acceptable working environments, it is preferable to incorporate the stabilizing solution with an azolymethylamine described in EP 504,609 and EP 519,190 or an N-methylolazole described in JP-A-4-362943 as formaldehyde substitute compounds and to make the magenta coupler bi-equivalent for the purpose of utilizing a solution of a surface active agent free of a formaldehyde-based image stabilizer.

**[0235]** Meanwhile, in order to reduce the amount of dusts adhering to the magnetic recording layer coated on the light-sensitive material, the stabilizing solution described in JP-A-6-289559 may be preferably used.

**[0236]** The quantity of replenisher of washing water or of the stabilizing solution is 80 to 1,000 mL, preferably 100 to 500 mL, and most preferably 150 to 300 mL per  $m^2$  of the light-sensitive material both from securing the water-washing or stabilizing function and from the reduction of waste solution in view of the environmental preservation. In the processing which is performed with the above-mentioned quantity of replenisher, it is preferable to use a known mildewproofing agent, such as thiabendazole, 1,2-benzisothiazoline-3-one or 5-chloro-2-methylisothiazoline-3-one, an antibiotic, such as gentamycin, and deionized water which has been deionization-treated with an ion-exchange resin in order to prevent the growth of bacteria or mildew. The use of a combination of deionized water with an antibacteria agent or an antibiotic is more effective.

**[0237]** Furthermore, it is desirable to reduce the amount of replenisher by the implementation of the reverse osmosis of the liquid inside the water-washing or stabilizing solution tank as described in JP-A-3-46652, JP-A-3-53246, JP-A-3-55542, JP-A-3-121448 and JP-A-3-126030. In this case, the reverse osmosis membrane is preferably a low-pressure reverse osmosis membrane.

**[0238]** In the processing of the present invention, it is particularly preferable to compensate for the evaporation of the processing solutions in accordance with the method described in Journal of Technical Disclosure No. 94-4992 of The Japan Institution of Innovation and Invention (hereinafter abbreviated as JIII). In particular, it is desirable to com-

compensate for the evaporation based on the Equation (1) on page 2. by use of the temperature and humidity information in the environment where the process is placed. The water to be used to compensate for evaporation is preferably taken from a replenishment tank to the water-washing bath, and the replenishing water is preferably deionized water.

[0239] The processing agents described in the above-mentioned Journal of Technical Disclosure, page 3, right column, line 15 to page 4, left column, line 32 are desirable for use in the present invention. A desirable processor using these processing agents is the film processor described in the above-mentioned Journal of Technical Disclosure, page 3, right column, lines 22 to 28.

[0240] Concrete examples of the desirable processing agents, automatic processors and methods for compensating for evaporation are described in the above-mentioned Journal of Technical Disclosure, page 5 right column, line 11 to page 7, right column, final line.

[0241] The supply form of a processing agent to be used in the present invention can be any of a liquid having the concentration of a solution in use, a concentrated liquid, a granule, a powder, a pellet, a paste and an emulsion. Examples of these processing agents are a liquid contained in a low-oxygen-permeability vessel disclosed in JP-A-63-17453, vacuum-packaged powders or granules disclosed in JP-A-4-19655 and JP-A-4-230748, granules containing a water-soluble polymer disclosed in JP-A-4-221951, pellets disclosed in JP-A-51-61837 and JP-A-6-102628, and a processing agent in the form of a paste disclosed in PCT National Publication No. 57-500485. Any of these forms can be preferably used. However, in respect of simplicity in use, the use of a liquid already prepared to have a concentration in use is preferable.

[0242] The material of vessels containing these processing agents can be any of polyethylene, polypropylene, polyvinylchloride, polyethylene terephthalate and nylon. These materials can be used singly or in the form of a composite material. These materials are so selected as to meet the level of a necessary oxygen permeability. Low-oxygen-permeability materials are suited to a solution such as a color developing solution which is readily oxidized. Practical examples are polyethylene terephthalate and a composite material of polyethylene and nylon. The thickness of a vessel made from any of these materials is 500 to 1,500  $\mu\text{m}$ . The oxygen permeability is preferably 20  $\text{mL/m}^2 \cdot 24 \text{ hrs. atm}$  or less.

[0243] The processing solution for the color reversal film to be used in the present invention is described below. The detail of the processing technique for a color reversal film is described in Journal of Known Technologies No. 6 (April 1, 1991, issued from ASTECH Co., Ltd.), page 1, line 5 to page 10, line 5 and page 15, line 8 to page 24, line 2. Any of these techniques can be preferably used in the present invention.

[0244] In the processing of the color reversal film, the control bath or the final bath contains the image stabilizing agent. Among examples of these image stabilizing agents which are formalin, sodium formaldehydebisulfite and N-methylolazole, preferable is sodium formaldehydebisulfite or an N-methylolazole, N-methyloltriazole in particular, from the viewpoint of working environments. Further, the techniques, which were stated previously concerning the color developing solution, bleaching solution, fixing solution and washing water for the processing of color negative film can also be preferably used for the processing of the color reversal film.

[0245] On the basis of the above description, preferred processing agents for color reversal films include E-6 Processing Agent manufactured by Eastman Kodak Co., Ltd. and CR-56 Processing Agent manufactured by Fuji Film Co., Ltd.

[0246] Then, a magnetic recording layer used in the present invention is described below.

[0247] The magnetic recording layer used in the present invention is formed by coating the surface of a support with an aqueous or organic solvent-based coating solution which is prepared by dispersing magnetic grains in a binder.

[0248] The magnetic grains used in the present invention can be ferromagnetic iron oxide such as  $\gamma \text{Fe}_2\text{O}_3$ , Co-deposited  $\gamma \text{Fe}_2\text{O}_3$ , Co-deposited magnetite, Co-containing magnetite, ferromagnetic chromium dioxide, a ferromagnetic metal, a ferromagnetic alloy, Ba ferrite of a hexagonal system, Sr ferrite, Pb ferrite and Ca ferrite. Co-deposited ferromagnetic iron oxide such as Co-deposited  $\gamma \text{Fe}_2\text{O}_3$  is preferable. The grain can take the shape of any of, e.g., a needle, a rice grain, a sphere, a cube and plate. A specific surface area is preferably 20  $\text{m}^2/\text{g}$  or more, and more preferably 20  $\text{m}^2/\text{g}$  or more as  $S_{\text{BET}}$ .

[0249] The saturation magnetization ( $\sigma_s$ ) of the ferromagnetic substance is preferably  $3.0 \times 10^4$  to  $3.0 \times 10^5 \text{ A/m}$ , and most preferably  $4.0 \times 10^4$  to  $2.5 \times 10^5 \text{ A/m}$ . A surface treatment can be performed for the ferromagnetic grains by use of silica and/or alumina or an organic material. Also, the surface of the ferromagnetic-grains can be treated with a silane coupling agent or a titanium coupling agent as described in JP-A-6-161032. Ferromagnetic grains, whose surface is coated with an inorganic or organic substance, described in JP-A-4-259911 and JP-A-5-81652 can also be used.

[0250] As the binder together with the magnetic grains, it is possible to use a thermoplastic resin, a thermosetting resin, a radiation-curable resin, a reactive resin, an acid-, alkali- or bio-degradable polymer, a natural polymer (e.g., a cellulose derivative and a saccharide derivative) and their mixtures described in JP-A-219569. Tg of the resin is  $-40^\circ\text{C}$  to  $300^\circ\text{C}$ , and its weight average molecular weight is 2,000 to 1,000,000. Examples of the resin are vinyl copolymer, cellulose derivatives, such as cellulose diacetate, cellulose triacetate, cellulose acetatepropionate, cellulose acetatebutylate and cellulose tripropionate, an acrylic resin, and a polyvinylacetal resin. Gelatine is also preferable. Cellulose

di(tri)acetate is particularly preferable. The binder can be hardened by the addition of an epoxy, aziridine, or isocyanate crosslinking agent. Examples of the isocyanate crosslinking agent include isocyanates, such as tolylenediisocyanate, 4,4'-diphenylmethanediisocyanate, hexamethylenediisocyanate and xylylenediisocyanate, reaction products of these isocyanates and polyalcohols (e.g., a reaction product of 3 mols of tolylenediisocyanate and 1 mol of trimethylolpropane), and a polyisocyanate produced by condensation of any of these isocyanates. These examples are described in, e.g., JP-A-6-59357.

**[0251]** As a method for dispersing the magnetic substance in the binder, as described in JP-A-6-35092, the use of a kneader, a pin-type mill or an annular mill is preferable, and a combination of them is also preferable. Dispersants described in JP-A-5-088283 and other known dispersants can be used. The thickness of the magnetic recording layer is 0.1 to 10  $\mu\text{m}$ , preferably 0.2 to 5  $\mu\text{m}$ , and more preferably 0.3 to 3  $\mu\text{m}$ . The weight ratio of the magnetic grains to the binder is preferably 0.5:100 to 60:100, and more preferably 1:100 to 30:100. The coating amount of the magnetic grains is 0.005 to 3  $\text{g}/\text{m}^2$ , preferably 0.01 to 2  $\text{g}/\text{m}^2$ , most preferably 0.02 to 0.5  $\text{g}/\text{m}^2$ . The transmission yellow density of the magnetic recording layer is preferably 0.01 to 0.50, more preferably 0.03 to 0.20, and most preferably 0.04 to 0.15. The magnetic recording layer can be formed in the whole area of, or in the shape of stripes on, the back surface of a photographic support by coating or printing. The magnetic recording layer can be formed by any coating method using, e.g., an air doctor, a blade, an air knife, squeezing, impregnation, a reverse roll, a transfer roll, gravure, kissing, casting, spray, dipping, a bar or extrusion. A coating solution described in JP-A-5-341436 is preferable.

**[0252]** The magnetic recording layer may have additional functions such as improvement of lubricating property, adjustment of curling, electrostatic charge prevention, adhesion prevention and polish of head. Alternatively, an additional functional layer may be formed which performs these functions. A preferable polishing agent contains at least one type of aspherical inorganic grains which have a Mohs hardness of 5 or more. The composition of the aspherical inorganic grain is preferably an oxide, such as aluminum oxide, chromium oxide, silicon dioxide and titanium dioxide, carbide, such as silicon carbide and titanium carbide, or a fine powder of diamond. The surfaces of the grains constituting these polishing agents can be treated with a silane coupling agent or a titanium coupling agent. These grains can be added to the magnetic recording layer, or the magnetic recording layer can be overcoated with a layer containing these grains (e.g., as a protective layer or a lubricating layer). The binder to be used together with the grains can be of any of those described above and is preferably the same binder as in the magnetic recording layer. Light-sensitive materials having the magnetic recording layer are described in U.S. Patents 5,336,589; 5,250,404; 5,229,259 and 5,215,874, and EP 466,130.

**[0253]** A polyester support to be used in the present invention is described below. Details of the polyester support, light-sensitive materials, treatment, cartridges and examples are described in Journal of Technical Disclosure No. 94-6,023 (JIII; March 15, 1994). The polyester used in the present invention is made up of a diol and an aromatic dicarboxylic acid as essential components. Examples of the aromatic dicarboxylic acid include 2,6-, 1,5-, 1,4- and 2,7-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid and phthalic acid. Examples of the diol include diethyleneglycol, triethyleneglycol, cyclohexanedimethanol, bisphenol A and bisphenol. Examples of the polymer are homopolymers such as polyethylene terephthalate, polyethylene naphthalate and polycyclohexanedimethanol terephthalate. The polyester containing 50 to 100 mol% of 2,6-naphthalenedicarboxylic acid is particularly preferable. Polyethylene 2,6-naphthalate is most preferable among these polymers. The average molecular weight ranges between 5,000 and 200,000. Tg of the polyesters for use in the present invention is 50°C or higher, preferably 90°C or higher.

**[0254]** In order to make the polyester support more resistant to curling, the polyester support is heat-treated at a temperature within the range of from 40°C to less than Tg, more preferably at a temperature within the range of from Tg - 20°C to less than Tg. The heat treatment can be performed at a fixed temperature within this range or can be performed together with cooling. The heat-treatment time is 0.1 to 1,500 hours, more preferably 0.5 to 200 hours. The heat treatment can be performed for a roll-like support or while the support is conveyed in the form of a web. Fine undulations (e.g., coating the surface with electroconductive inorganic fine grains such as  $\text{SnO}_2$  or  $\text{Sb}_2\text{O}_5$ ) may be given to the surface to improve the surface condition. It is also desirable to knurl and slightly raise the end portion, thereby preventing the shape of cut portion of the core from being transmitted. These heat treatments can be performed at any stage, for example, after support film formation, after surface treatment, after back layer coating (e.g., an antistatic agent or lubrication agent) and after the application of an undercoat. A preferable timing for the heat treatment is after the application of the antistatic agent.

**[0255]** An ultraviolet absorbent may be incorporated into this polyester. Also, the prevention of light piping can be achieved by incorporating the polyester with a dye or pigment, such as Diaresin manufactured by Mitsubishi Chemical Industries, Ltd. or Kayaset manufactured by Nippon Kayaku Co., Ltd., which is commercially available as an additive to polyester.

**[0256]** In the present invention, it is preferable to perform a surface treatment of the support in order to increase the bonding strength between the support and the light-sensitive material constituting layers. Examples of the surface treatment are surface activating treatments which include a chemical treatment, a mechanical treatment, a corona discharge treatment, a flame treatment, an ultraviolet treatment, a high-frequency treatment, a glow discharge treat-

ment, an active plasma-treatment, a laser treatment, a mixed acid treatment and an ozone oxidation treatment. Preferred surface treatments are the ultraviolet irradiation treatment, the flame treatment, the corona treatment and the glow treatment.

**[0257]** The undercoat may consist of a single layer or two or more layers. Examples of the binder for the undercoat layer include a copolymer produced by using, as a starting material, a monomer selected from the group consisting of vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid, maleic anhydride and the like. Other examples include polyethyleneimine, an epoxy resin, grafted gelatin, nitrocellulose and gelatin. Resorcin and p-chlorophenyl are examples of a compound which swells the support. Examples of a gelatin hardener to be added to the undercoat layer include chromium salts (e.g., chromium alum), aldehydes (e.g., formaldehyde and glutaraldehyde), isocyanates, active halogenated compounds (e.g., 2,4-dichloro-6-hydroxy-s-triazine), epichlorohydrin resins and active vinylsulfones. The undercoat layer may contain  $\text{SiO}_2$ ,  $\text{TiO}_2$ , inorganic fine grains or fine grains of a polymethyl methacrylate copolymer (0.01 to 10  $\mu\text{m}$ ) as a matting agent.

**[0258]** In the present invention, an antistatic agent is preferably used. Examples of the antistatic agent include polymers containing carboxylic acid group, carboxylate group or a sulfonate group, cationic polymers and ionic surfactant compounds.

**[0259]** It is most preferable to use as the antistatic agent at least one finely-divided crystalline metal oxide which is selected from the group consisting of  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  and which has a volume resistivity of  $10^7 \Omega\cdot\text{cm}$  or less, more preferably  $10^5 \Omega\cdot\text{cm}$  or less, and a grain size of 0.001 to 1.0  $\mu\text{m}$ , fine grains of composite oxides (e.g., Sb, P, B, In, S, Si and C) of these metal oxides, fine grains of sol metal oxides, or fine grains of composite oxides of these sol metal oxides.

**[0260]** The content in the light-sensitive material is preferably 5 to 500  $\text{mg}/\text{m}^2$ , and most preferably 10 to 350  $\text{mg}/\text{m}^2$ . The weight ratio of an electroconductive crystalline oxide or its composite oxide to the binder is preferably 1/300 to 100/1, and more preferably 1/100 to 100/5.

**[0261]** The light-sensitive material of the present invention preferably has a slip property. Slip agent-containing layers are preferably formed on the surfaces of both a light-sensitive layer and a back layer. A preferable slip property is indicated by a coefficient of kinetic friction of 0.01 to 0.25. This value represents the value that is obtained when a sample is conveyed at a speed of 60 cm/min while keeping contact with a stainless steel ball having a diameter of 5 mm (25°C, 60% RH). In this evaluation, a value of nearly the same level is obtained even when the stainless steel ball is replaced with the surface of a light-sensitive layer.

**[0262]** Examples of the slip agent usable in the present invention are polyorganosiloxanes, higher fatty acid amides, metals salts of higher fatty acids, and esters of higher fatty acids and higher alcohols. Examples of the polyorganosiloxanes include polydimethylsiloxane, polydiethylsiloxane, polystyrylmethylsiloxane and polymethylphenylsiloxane. A layer to which the slip agent is added is preferably the outermost emulsion layer or the back layer. Polydimethylsiloxanes or esters having a long-chain alkyl group are particularly preferable.

**[0263]** The light-sensitive material of the present invention preferably contains a matting agent. Although the matting agent can be added to either the emulsion surface or the back surface, it is most preferably added to the outermost layer on the side having the emulsion layer. The matting agent can be either soluble or insoluble in the processing solutions, and the use of a combination of both types of the matting agents is preferable. Preferable examples are polymethylmethacrylate grains, poly(methylmethacrylate/methacrylic acid = 9:1 or 5/5 (molar ratio)) grains and polystyrene grains. The grain size is preferably 0.8 to 10  $\mu\text{m}$ , and a narrow grain size distribution is preferable. It is preferable that 90% or more by number of all of the grains have grain sizes of 0.9 to 1.1 times the average grain size. To increase the matting effect, it is preferable to simultaneously add fine grains having a grain size of 0.8  $\mu\text{m}$  or less, examples of which include polymethylmethacrylate grains (0.2  $\mu\text{m}$ ), poly(methylmethacrylate/methacrylic acid = 9/1 (molar ratio)) grains (0.3  $\mu\text{m}$ ), polystyrene grains (0.25  $\mu\text{m}$ ) and colloidal silica (0.03  $\mu\text{m}$ ).

**[0264]** A film cartridge to be used in the present invention is described below. The principal material of the cartridge to be used in the present invention can be a metal or synthetic plastic.

**[0265]** Examples of preferable plastic materials include polystyrene, polyethylene, polypropylene and polyphenylene ether. The cartridge of the present invention can also contain various antistatic agents.

**[0266]** For this purpose, carbon black, metal oxide grains, nonionic, anionic, cationic or betaine surfactants, or polymers can be preferably used. These cartridge subjected to the antistatic treatment are described in JP-A-1-312537 and JP-A-312538. It is particularly preferable that the resistance be  $10^{12} \Omega$  or less at 25°C and 25% RH. Commonly, plastic cartridges are manufactured by using plastics into which carbon black or pigments are incorporated to give a light-shielding property. The cartridge size can be a presently available 135 size. For the purpose of down-sizing the cameras, it is effective to decrease the diameter of 25-mm cartridge of 135 size to 22 mm or less. The volume of a cartridge case is 30  $\text{cm}^3$  or less, preferably 25  $\text{cm}^3$  or less. The weight of the plastic used in the cartridge and the cartridge case is preferably 5 to 15 g.

**[0267]** Furthermore, a cartridge which feeds a film by rotating a spool can be used in the present invention. It is also possible to use a structure in which a film leader is housed in a cartridge main body and fed through a port of the

cartridge to the outside by rotating a spool shaft in the film feed direction. These structures are disclosed in U.S. Patents 4,834,306 and 5,226,613. Photographic films to be used in the present invention can be so-called raw films before being developed or developed photographic films. Also, raw and developed photographic films can be accommodated in the same new cartridge or in different cartridge.

**[0268]** The color photographic light-sensitive material of the present invention is also suitable as a negative film for use in Advanced Photo System (hereinafter referred to AP system) and examples of which are formed by processing films in AP system format like NEXIA A, NEXIA F and NEXIA H (in this order; ISO 200/100/400) manufactured by Fuji Photographic Film, Ltd. (hereinafter referred to Fuji Film) and accommodating them in an exclusive cartridge. These cartridge films for use in AP system are used by charging into cameras for AP system such as Epion Series (such as Epion 300Z) manufactured by Fuji Film. In addition, the color, photographic light-sensitive material of the present invention is also suitable for films with a lens such as "Fiji Color Quick Snap" manufactured by Fuji Film.

**[0269]** The films photographed by them are printed in Mini Lab System through the following steps.

- (1) Receiving (Receiving of the exposed cartridge film from a customer)
- (2) Detachment step (The film is transferred from the cartridge to an intermediate cartridge for developing step)
- (3) Film development
- (4) Reattachment step (The developed negative film is returned to the original cartridge)
- (5) Print (C/H/P three types of prints and an index print are printed successively and automatically printed on color print papers (preferably SUPER FA8 manufactured by Fuji Film).
- (6) Collation and shipment (The cartridge and the index print are collated using ID number and shipped together with the print).

**[0270]** The preferable detacher used in detachment step and the preferable reattacher used in reattachment step are DT200/DT100 and AT200/AT100 manufactured by Fuji Film, respectively.

**[0271]** The present invention will be explained in more detail below by reference to the following example. However, the present invention is not limited to this example.

Sample 101:

**[0272]** Multiple layers having the compositions presented below were coated on an undercoated cellulose triacetate film support to make the sample 101 as a multilayered color sensitive material.

#### Compositions of sensitive layers

**[0273]** The main materials used in the individual layers are classified as follows.

ExC	Cyan coupler	UV	Ultraviolet absorbent
ExM	Magenta coupler	HBS	High-boiling organic solvent
ExY	Yellow coupler	H	Gelatin hardener
ExS	Sensitizing dye		

The various chemical compositions are given after the examples.

**[0274]** The number corresponding to each component indicates the coating amount in units of g/m<sup>2</sup>. The coating amount of a silver halide is represented by the amount of silver. The coating amount of each sensitizing dye is represented in units of mols per mol of a silver halide in the same layer.

#### Sample 101

**[0275]**

1st layer (Antihalation layer)	
Black colloidal silver	silver 0.18
Gelatin	1.40
ExM-1	0.11
HBS-1	0.16



# EP 1 083 461 A1

2nd layer (Interlayer)	
ExC-2	0.030
UV-1	0.020
UV-2	0.020
UV-3	0.060
HBS-1	0.05
HBS-2	0.020
Polyethylacrylate latex	0.080
Gelatin	0.90

3rd layer (Low-speed red-sensitive emulsion layer)	
Emulsion A	silver 0.23
Emulsion B	silver 0.23
ExS-1	$5.0 \times 10^{-4}$
ExS-2	$1.8 \times 10^{-5}$
ExS-3	$5.0 \times 10^{-4}$
ExC-1	0.050
ExC-3	0.030
ExC-4	0.14
ExC-5	$3.0 \times 10^{-3}$
ExC-7	$1.0 \times 10^{-3}$
ExC-8	0.010
Cpd-2	0.005
HBS-1	0.10
Gelatin	0.90

4th layer (Medium-speed red-sensitive emulsion layer)	
Emulsion C	silver 0.70
ExS-1	$3.4 \times 10^{-4}$
ExS-2	$1.2 \times 10^{-5}$
ExS-3	$4.0 \times 10^{-4}$
ExC-1	0.15
ExC-2	0.060
ExC-4	0.050
ExC-5	0.010
ExC-8	0.010
Cpd-2	0.023
HBS-1	0.11
Gelatin	0.60

5th layer (High-speed red-sensitive emulsion layer)	
Emulsion D	silver 1.62
ExS-1	$2.4 \times 10^{-4}$
ExS-2	$1.0 \times 10^{-5}$
ExS-3	$3.0 \times 10^{-4}$
ExC-1	0.10
ExC-3	0.050

# EP 1 083 461 A1

(continued)

5th layer (High-speed red-sensitive emulsion layer)	
ExC-5	$2.0 \times 10^{-3}$
ExC-6	0.010
ExC-8	0.010
Cpd-2	0.025
HBS-1	0.20
HBS-2	0.10
Gelatin	1.30

6th layer (Interlayer)	
Cpd-1	0.090
HBS-1	0.05
Polyethylacrylate latex	0.15
Gelatin	1.10

7th layer (Low-speed green-sensitive emulsion layer)	
Emulsion E	silver 0.24
Emulsion F	silver 0.24
ExS-4	$4.0 \times 10^{-5}$
ExS-5	$1.8 \times 10^{-4}$
ExS-6	$6.5 \times 10^{-4}$
ExM-1	$5.0 \times 10^{-3}$
ExM-2	0.28
ExM-3	0.086
ExM-4	0.030
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.85

8th layer (Medium-speed green-sensitive emulsion layer)	
Emulsion G	silver 0.94
ExS-4	$2.0 \times 10^{-5}$
ExS-5	$1.4 \times 10^{-4}$
ExS-6	$5.4 \times 10^{-4}$
ExM-2	0.14
ExM-3	0.045
ExM-5	0.020
ExY-1	$7.0 \times 10^{-3}$
ExY-4	$2.0 \times 10^{-3}$
ExY-5	0.020
HBS-1	0.16
HBS-3	$8.0 \times 10^{-3}$
Gelatin	0.80

# EP 1 083 461 A1

9th layer (High-speed green-sensitive emulsion layer)	
Emulsion H	silver 1.29
ExS-4	$3.7 \times 10^{-5}$
ExS-5	$8.1 \times 10^{-5}$
ExS-6	$3.2 \times 10^{-4}$
ExC-1	0.010
ExM-1	0.020
ExM-4	0.050
ExM-5	0.020
ExY-4	$5.0 \times 10^{-3}$
Cpd-3	0.050
HBS-1	0.13
HBS-2	0.05
Polyethylacrylate latex	0.26
Gelatin	1.45

10th layer (Yellow filter layer)	
Yellow colloidal silver	silver $7.5 \times 10^{-3}$
Cpd-1	0.13
Cpd-4	$7.5 \times 10^{-3}$
HBS-1	0.60
Gelatin	0.60

11th layer (Low-speed blue-sensitive emulsion layer)	
Emulsion I	silver 0.25
Emulsion J	silver 0.25
Emulsion K	silver 0.10
ExS-7	$8.0 \times 10^{-4}$
ExC-7	0.010
ExY-1	$5.0 \times 10^{-3}$
ExY-2	0.40
ExY-3	0.45
ExY-4	$6.0 \times 10^{-3}$
ExY-6,	0.10
HBS-1	0.30
Gelatin	1.65

12th layer(High speed blue-sensitive emulsion layer)	
Emulsion L	silver 1.30
ExS-7	$3.0 \times 10^{-4}$
ExY-2	0.15
ExY-3	0.06
ExY-4	$5.0 \times 10^{-3}$
Cpd-2	0.10
HBS-1	0.070
Gelatin	1.20

13th layer (1st protective layer)	
UV-2	0.10
UV-3	0.12
UV-4	0.30
HBS-1	0.10
Gelatin	2.50

14th layer (2nd protective layer)	
Emulsion M	silver 0.10
H-1	0.37
B-1 (diameter 1.7 $\mu\text{m}$ )	$5.0 \times 10^{-2}$
B-2 (diameter 1.7 $\mu\text{m}$ )	0.15
B-3	0.05
S-1	0.20
Gelatin	0.70

**[0276]** In addition to the above components, to improve shelf stability, processability, pressure resistance, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salt, lead salt, gold salt, platinum salt, iridium salt, palladium salt, and rhodium salt.

**[0277]** Cpd-4 was dispersed in the form of a solid in accordance with a method described in International Patent Application WO/88-4794.

**[0278]** Table 11 below shows the grain shapes and the like of the emulsions A to M used in the sample 201 described above.

TABLE 11

	Grain shape (halogen structure)	Average AgI content (%)	Inter-grain iodide distribution variation coefficient (%)
Emulsion A	Circular tabular (uniform structure)	0	-
B	Cubic (double structure with high iodide shell)	1.0	-
C	Tetradecahedral (triple structure with high iodide intermediate shell)	4.5	25
D	Hexagonal tabular (structure with high iodide outside)	2.0	16
E	Circular tabular (structure with high iodide outside)	1.0	-
F	Octahedral (double structure with high iodide core)	6.0	22
G	Tetradecahedral (triple structure with high iodide intermediate shell)	4.5	19
H	Hexagonal tabular (structure with high iodide central portion)	2.3	-
I	Circular tabular (structure with high iodide central portion)	2.0	15
J	Cubic (uniform structure)	1.0	10
K	Tetradecahedral (double structure with high iodide core)	18.0	8
L	Hexagonal tabular (structure with high iodide central portion)	2.3	-
M	Non-light sensitive fine grain (uniform structure)	1.0	-

(Continued)

TABLE 11

	Average grain size, equivalent-sphere diameter ( $\mu\text{m}$ )	Variation coefficient (%) of grain size	Diameter/thickness ratio
Emulsion A	0.45	15	5.5
B	0.20	8	1
C	0.85	18	1
D	1.10	17	7.5
E	0.45	15	3.0
F	0.25	8	1
G	0.85	19	1
H	0.95	18	7.0
I	0.45	15	6.0
J	0.30	8	1
K	0.80	18	1
L	1.80	20	8.0
M	0.04	15	1

[0279] In Table 11,

(1) The emulsions I to K were subjected to reduction sensitization during grain preparation by using thiourea dioxide and thiosulfonic acid in accordance with the embodiments in Jpn. Pat. Appln. KOKAI Publication No. 2-91938.

(2) The emulsions A to K were subjected to gold sensitization, sulfur sensitization, and selenium sensitization in the presence of the spectral sensitizing dyes described in the individual sensitive layers and sodium thiocyanate in accordance with the embodiments in Jpn. Pat. Appln. KOKAI Publication No. 3-237450.

(3) The preparation of tabular grains was performed by using low-molecular weight gelatin in accordance with the embodiments in Jpn. Pat. Appln. KOKAI Publication No. 1-158426.

(4) Dislocation lines as described in Jpn. Pat. Appln. KOKAI Publication No. 3-237450 were observed in tabular grains and regular crystal grains having a grain structure when a high-voltage electron microscope was used.

[0280] The couplers and additives in each layer were dispersed in a gelatin solution by a method shown in Table 12. addition methods for individual layers are shown in Table 13.

TABLE 12

Dispersion method	Method
A	Uniform aqueous solution of couplers, high-boiling point organic solvent(s), surfactant(s), NaOH, n-propanol, and other additive(s) is neutralized, precipitated, and dispersed
B	Uniform n-propanol solution of couplers, high-boiling point organic solvent(s), and other additive(s) is added to aqueous surfactant solution and precipitated and dispersed
C	Solution of couplers, high-boiling point organic solvent(s), surfactant(s), low-boiling point organic solvent(s), and other additive(s) and aqueous solution of gelatin and surfactants are mixed, stirred, and emulsified to disperse, and low-boiling point organic solvent(s) is removed by evaporation
D	Organic solvents are removed by washing or ultrafiltration after dispersion in method C

TABLE 13

Layer	Dispersion method	Average dispersed grain size [nm]
3 <sup>rd</sup> layer	C	133
4 <sup>th</sup> layer	C	130
5 <sup>th</sup> layer	D	40
7 <sup>th</sup> layer	C	135
8 <sup>th</sup> layer	C	60
9 <sup>th</sup> layer	A	40
11 <sup>th</sup> layer	C	125
12 <sup>th</sup> layer	B	80

Sample 102

[0281]

1st layer (Antihalation layer)	
Black colloidal silver	silver 0.18
Gelatin	1.40
ExM-1	0.11
HBS-1	0.16

# EP 1 083 461 A1

2nd layer (Interlayer)	
UV-1	0.020
UV-2	0.020
UV-3	0.060
HBS-1	0.05
HBS-2	0.020
Polyethylacrylate latex	0.080
Gelatin	0.90

3rd layer (Low-speed red-sensitive emulsion layer)	
Emulsion A	silver 0.26
Emulsion B	silver 0.23
ExS-1	$5.0 \times 10^{-4}$
ExS-2	$1.8 \times 10^{-5}$
ExS-3	$5.0 \times 10^{-4}$
ExC-1	0.071
ExC-3	0.045
ExC-4	0.21
Cpd-2	0.005
Cpd-3	0.005
HBS-1	0.10
Gelatin	0.90

4th layer (Medium-speed red-sensitive emulsion layer)	
Emulsion B	silver 0.18
Emulsion C	silver 0.18
ExS-1	$3.4 \times 10^{-4}$
ExS-2	$1.2 \times 10^{-5}$
ExS-3	$4.0 \times 10^{-4}$
ExC-1	0.11
ExC-4	0.038
Cpd-2	0.023
Cpd-3	0.023
HBS-1	0.11
Gelatin	0.60

5th layer (High-speed red-sensitive emulsion layer)	
Emulsion D	silver 2.18
ExS-1	$2.4 \times 10^{-4}$
ExS-2	$1.0 \times 10^{-5}$
ExS-3	$3.0 \times 10^{-4}$
ExC-1	0.062
ExC-3	0.050
ExC-6	0.012
Cpd-2	0.025
Cpd-3	0.025
HBS-1	0.20



# EP 1 083 461 A1

(continued)

5th layer (High-speed red-sensitive emulsion layer)	
HBS-2	0.10
Gelatin	1.30

6th layer (Interlayer)	
Cpd-1	0.090
HBS-1	0.05
Polyethylacrylate latex	0.15
Gelatin	1.10

7th layer (Low-speed green-sensitive emulsion layer)	
Emulsion E	silver 0.57
Emulsion F	silver 0.24
ExS-4	$4.0 \times 10^{-5}$
ExS-5	$1.8 \times 10^{-4}$
ExS-6	$6.5 \times 10^{-4}$
ExM-2	0.23
ExM-4	0.025
HBS-1	0.30
HBS-3	0.010
Gelatin	0.85

8th layer (Medium-speed green-sensitive emulsion layer)	
Emulsion F	silver 0.11
Emulsion G	silver 0.11
ExS-4	$2.0 \times 10^{-5}$
ExS-5	$1.4 \times 10^{-4}$
ExS-6	$5.4 \times 10^{-4}$
ExM-2	0.006
ExM-5	0.038
HBS-1	0.08
HBS-3	$4 \times 10^{-3}$
Gelatin	0.80

9th layer (High-speed green-sensitive emulsion layer)	
Emulsion H	silver 1.67
ExS-4	$3.7 \times 10^{-5}$
ExS-5	$8.1 \times 10^{-5}$
ExS-6	$3.2 \times 10^{-4}$
ExC-1	0.006
ExM-4	0.027
ExM-5	0.011
Cpd-3	0.050
HBS-1	0.08
HBS-2	0.03

# EP 1 083 461 A1

(continued)

9th layer (High-speed green-sensitive emulsion layer)	
Polyethylacrylate latex	0.26
Gelatin	1.45

10th layer (Yellow filter layer)	
Yellow colloidal silver	silver $7.5 \times 10^{-3}$
Cpd-1	0.13
Cpd-4	$7.5 \times 10^{-3}$
HBS-1	0.60
Gelatin	0.60

11th layer (Low-speed blue-sensitive emulsion layer)	
Emulsion I	silver 0.17
Emulsion J	silver 0.25
Emulsion K	silver 0.10
ExS-7	$8.0 \times 10^{-4}$
ExY-2	0.37
HBS-1	0.30
Gelatin	1.65

12th layer (Medium speed blue-sensitive emulsion layer)	
Emulsion J	silver 0.086
Emulsion K	silver 0.086
ExS-7	$8.0 \times 10^{-4}$
ExY-2	0.37
HBS-1	0.30
Gelatin	1.65

13th layer (High speed blue-sensitive emulsion layer)	
Emulsion L	silver 0.51
ExS-7	$3.0 \times 10^{-4}$
ExY-2	0.092
Cpd-2	0.10
HBS-1	0.23
Gelatin	1.20

14th layer (1st protective layer)	
UV-2	0.10
UV-3	0.12
UV-4	0.30
HBS-1	0.10
Gelatin	2.50

15th layer (2nd protective layer)	
Emulsion M	silver 0.10
H-1	0.37
B-1 (diameter 1.7 $\mu\text{m}$ )	$5.0 \times 10^{-2}$
B-2 (diameter 1.7 $\mu\text{m}$ )	0.15
B-3	0.05
S-1	0.20
Gelatin	0.70

**[0282]** In addition to the above components, to improve shelf stability, processability, pressure resistance, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salt, lead salt, gold salt, platinum salt, iridium salt, palladium salt, and rhodium salt.

**[0283]** Cpd-4 was dispersed in the form of a solid in accordance with a method described in International Patent Application WO/88-4794.

#### Sample 103

**[0284]** This was made in the same way as sample 102 except for the following.

**[0285]** In the 5<sup>th</sup> layer, the coating amount of HBS-1 and HBS-2 were changed from 0.20, 0.10 to 0.40, 0.20, respectively.

**[0286]** In the 9<sup>th</sup> layer, the coating amount of HBS-1 and HBS-2 were changed from 0.08, 0.03 to 0.16, 0.06, respectively.

**[0287]** In the 13<sup>th</sup> layer, the coating amount of HBS-1 was changed from 0.23 to 0.46, respectively.

#### Sample 104

**[0288]** This was made in the same way as sample 102 except for the following.

**[0289]** In the 5<sup>th</sup> layer, the coating amount of HBS-1 and HBS-2 were changed from 0.20, 0.10 to 0.80, 0.40, respectively.

**[0290]** In the 9<sup>th</sup> layer, the coating amount of HBS-1 and HBS-2 were changed from 0.08, 0.03 to 0.32, 0.12, respectively.

**[0291]** In the 13<sup>th</sup> layer, the coating amount of HBS-1 was changed from 0.23 to 0.46, respectively.

#### Sample 105

**[0292]** This was made in the same way as sample 104 except for the following.

**[0293]** In the 5<sup>th</sup> layer, the coating amount of ExC-1, ExC-3, and ExC-6 were changed from 0.062, 0.050, 0.012 to 0.020, 0, 0.004, respectively.

**[0294]** In the 9<sup>th</sup> layer, the coating amount of ExC-1, ExM-4, and ExM-5 were changed from 0.006, 0.027, 0.011 to 0.001, 0.006, 0.002, respectively.

**[0295]** In the 13<sup>th</sup> layer, the coating amount of ExY-2 was changed from 0.092 to 0.02.

**[0296]** The characteristic value of the developed color negative film in the standard development condition was shown in Table.1. The coupler/oil ratio is summarized in Table.2.

#### Development processing

**[0297]** The processing steps and compositions of the processing solution are shown below.

## EP 1 083 461 A1

(Processing)

Processing 1:

**[0298]**

Step	Time	Temp.	Rate of Replenishment*	Tank Volume
Color development	3 min 5 sec	38.0°C	23 ml	17 liter
Bleach	50 sec	38.0°C	5 ml	5 liter
Blix	50 sec	38.0°C	-	5 liter
Fixing	50 sec	38.0°C	16 ml	5 liter
Washing	30 sec	38.0°C	34 ml	3.5 liter
Stabilization (1)	20 sec	38.0°C	-	3 liter
Stabilization (2)	20 sec	38.0°C	20 ml	3 liter
Drying	1 min 30 sec	60°C		

Note:

\* Per 1.1 meter of a 35 mm wide photographic material (corresponding to a 24-exposure roll)

**[0299]** Stabilization was carried out in a counter-current system from (2) toward (1). All the overflow from the washing tank was introduced into the fixing bath. A cutout was made at the upper part of the bleaching tank and the fixing tank in the automatic developing machine so that all the overflow from these tanks might flow into the blix bath. The amount of processing solutions carried over to the next bath, i.e., the developer carried over to the bleaching bath, the bleaching solution carried over to the blix step, the blix bath carried over to the fixing step, and the fixer carried over to the washing step was 2.5 ml, 2.0 ml, 2.0 ml, and 2.0 ml, respectively, per 1.1 m x 35 mm width. The cross-over time between every two steps was 6 seconds, and it was included in the processing time of the former step.

**[0300]** Compositions of the processing solutions used are described below.

Color Developer:

**[0301]**

	Running Solution (g)	Replenisher (g)
Diethylenetriaminepentaacetic acid	2.0	2.0
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0	2.0
Sodium sulfite	3.9	5.1
Potassium carbonate	37.5	39.0
Potassium bromide	1.4	0.4
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.4	3.3
2-Methyl-4-[N-ethyl-N-( $\beta$ -hydroxyethyl)amino]aniline sulfate	4.5	6.0
Water to make	1.0 liter	1.0 liter
pH (adjusted with potassium hydroxide and sulfuric acid)	10.05	10.15

## EP 1 083 461 A1

### Bleaching Solution:

#### [0302]

	Running Solution (g)	Replenisher (g)
Ammonium 1,3-diaminopropanetetraacetate ferrate monohydrate	130	195
Ammonium bromide	70	105
Ammonium nitrate	14	21
Hydroxyacetic acid	25	38
Acetic acid	40	60
Water to make	1.0 liter	1.0 liter
pH (adjusted with aqueous ammonia)	4.4	4.0

### Blix Bath:

[0303] A 15.85 (by volume) mixture of the above bleaching solution and the following fixer (pH=7.0).

### Fixer:

#### [0304]

	Running Solution (g)	Replenisher (g)
Ammonium sulfite	19	57
Ammonium thiosulfate aqueous solution (700 g/l)	280 ml	840 ml
Imidazole	15	45
Ethylenediaminetetraacetic acid	15	45
Water to make	1.0 liter	1.0 liter
pH (adjusted with aqueous ammonia and acetic acid)	7.4	7.45

### Washing Solution:

[0305] Prepared by passing tap water through a mixed bed column packed with an H type strongly acidic cation-exchange resin AMBERLITE IR-120B, produced by Rohm & Haas Co., and an OH type strongly basic anion-exchange resin AMBERLITE IRA-400, produced by Rohm & Haas Co., to reduce the Ca and Mg ions each to 3 mg/l or lower and then adding to the treated water 20 mg/l of sodium sulfate. The resulting washing solution had a pH between 6.5 and 7.5.

### Stabilizer:

[0306] Common to running solution and replenisher:

Sodium p-toluenesulfinate	0.03 g
Polyoxyethylene p-monononylphenyl ether (average degree of polymerization: 10)	0.2 g
Di-sodium ethylenediaminetetraacetate	0.05 g
1,2,4-Triazole	1.3 g
1,4-Bis(1,2,4-triazol-1-ylmethyl)piperazine	0.75 g
Water to make	1.0 liter
pH	8.5

### 3. Image processing and output device

**[0307]** To input the developed image, to convert into an electric picture signal, and to do the image processing, we used the high-speed scanner/image workstation SP-1000 (made of the Fuji Photo Film Co., Ltd.) which is available on the market. In order to output and obtain the color print, Laser printer/paper processor LP-1000P (made of the Fuji Photo Film Co., Ltd. was used.

**[0308]** Moreover, for the comparison, Color printer/paper processor PP728A of a surface exposure method (Fuji mini-lab champion, made of Fuji Photo Film Co., Ltd.) was used. The printer of this device exposes a whole image simultaneously. And the printing is done on the color paper through the developed color negative film. It is a method usually done in a market to control the color balance and the print concentration by controlling the filter. The color paper (Fuji color paper super FA5, made by the Fuji Photo Film Co., Ltd.) is used. The development is CP47L of a general prescription (made of for the color paper by the Fuji Photo Film Co., Ltd.).

### 4. Test result

**[0309]** The image is exposed to the roll film processed to 1.1 m length and a width of 35 mm for sample 101-106. The object which contained Macbeth chart was exposed by using sample 101-106. The exposure conditions are -3 stops, normal, +3 stops and +6 stops.

**[0310]** The print was obtained by using Fuji color paper super-FA5 (made of the Fuji Photo Film Co., Ltd.), the above-mentioned high-speed scanner/image workstation SP-1000 (made of the Fuji Photo Film Co., Ltd.), and the laser printer/paper processor LP-1000P (made of the Fuji Photo Film Co., Ltd.).

**[0311]** The evaluation result of the print was summarized in the table. Moreover, the result in the print which was obtained by the whole image exposure simultaneously was indicated in Table in case of sample 101.

**[0312]** The evaluation results are summarized in Table3. The granularity results are shown. Regarding the evaluation, the point 5 is given to the sample 101 in the normal exposure condition, and the point 10 is given to the worst sample in this test. The concentration in the shadow part was relatively shown in Table4 by the difference from the standard exposure print (in Table4, shown as N).

**[0313]** As mentioned above, the difference from the standard condition becomes slightly small in both the under exposure and the over exposure by doing a digital image processing. In this case, the granularity was found to be worse in the under-exposure condition. When 102 ~ 105 are compared in digital processing with 101, the improvement is clear in the density reproduction. The granularity especially in the under-exposure condition shows a clear improvement, using this invention. And when 105 is compared with other samples, the improvement is clear and more preferable in both the gradation reproduction and the granularity. The sample 105 was also processed to the shape of "Films with a lens, Fuji Film's Quick Snap". The results of this shape showed the same as the usual roll film.

Table 14

Characteristic Values						
Sample Number	Dmin			T1-T0		
	Blue	Green	Red	Blue	Green	Red
101 (reference)	0.88	0.59	0.25	-0.22	-0.21	-0.20
102 (reference)	0.25	0.21	0.21	-0.22	-0.21	-0.21
103 (invention)	0.25	0.21	0.21	-0.22	-0.21	-0.22
104 (invention)	0.25	0.21	0.21	-0.22	-0.21	-0.23
105 (invention)	0.25	0.21	0.21	0.09	0.11	0.11

Table 15

Coupler/Oil ratio									
Sample Number	RL			GL			BL		
	R-u	R-m	R-o	G-u	G-m	G-o	B-u	B-m	B-o
101 (reference)	2.34	2.55	0.57	1.34	1.45	0.58	3.24	xxx	3.07
102 (reference)	3.26	1.35	0.41	0.82	0.52	0.40	1.23	1.23	0.40

# EP 1 083 461 A1

Table 15 (continued)

Coupler/Oil ratio									
Sample Number	RL			GL			BL		
	R-u	R-m	R-o	G-u	G-m	G-o	B-u	B-m	B-o
103 (invention)	3.26	1.35	0.20	0.82	0.52	0.20	1.23	1.23	0.20
104 (invention)	3.26	1.35	0.10	0.82	0.52	0.10	1.23	1.23	0.20
105 (invention)	3.26	1.35	0.02	0.82	0.52	0.02	1.23	1.23	0.04

Table 16

Granularity					
		Exposure			
Sample	Treatment	-3 stops	N	+3 stops	+6 stops
101 (reference)	Surface exposure	8	5	5	5
101 (reference)	Digital treatment	10	5	5	5
102 (reference)	Digital treatment	8	5	5	5
103 (invention)	Digital treatment	7	5	5	5
104 (invention)	Digital treatment	6	4	5	5
105 (invention)	Digital treatment	6	4	5	5

Table 17

Sample	Exposure														
	-3 stops			N			+3 stops			+6 stops					
	B	G	R	B	G	R	B	G	R	B	G	R	B	G	R
Treatment															
101(reference)															
Surface exposure	-0.10	-0.08	-0.08	0	0	0	-0.15	-0.14	-0.14	-0.30	-0.31	-0.30	-0.30	-0.31	-0.30
101(reference)															
Digital treatment	-0.05	-0.04	-0.04	0	0	0	-0.10	-0.09	-0.09	-0.25	-0.26	-0.25	-0.25	-0.26	-0.25
102(reference)															
Digital treatment	0	0	0	0	0	0	-0.09	-0.08	-0.08	-0.22	-0.24	-0.22	-0.22	-0.24	-0.22
103(invention)															
Digital treatment	0	0	0	0	0	0	-0.09	-0.08	-0.08	-0.22	-0.24	-0.22	-0.22	-0.24	-0.22
104(invention)															
Digital treatment	0	0	0	0	0	0	-0.09	-0.08	-0.08	-0.22	-0.24	-0.22	-0.22	-0.24	-0.22
105(invention)															
Digital treatment	0	0	0	0	0	0	-0.01	-0.01	-0.01	-0.01	-0.02	-0.01	-0.01	-0.02	-0.01



Brief explanation of Figs.

**[0314]**

- 5 [Fig.1]  
Block diagram which shows the entire flow of this invention, method of forming image of this invention, and the basic composition of device
- [Fig.2]  
Block diagram by which basic composition of image reproduction system.
- 10 [Fig.3]  
Fig. which shows external form of image reproduction by system in one execution.
- [Fig.4]  
Fig. which shows outline of transmittance type image reader.
- [Fig.5]  
Block diagram by which a part of composition of image processing device 5 in Fig.2 is shown.
- 15 [Fig.6]  
Block diagram by which other parts not shown in Fig.5 of image processing device 5 are shown.
- [Fig.7]  
Block diagram by which details of the first frame memory unit, the second frame memory unit, and the third frame memory unit in Fig.5 are shown.
- 20 [Fig.8]  
Block diagram by which details of the first image processing means in Fig.6 are shown.
- [Fig.9]  
Fig. which shows outline of image output device shown in Fig.2.
- 25 [Fig.10]  
Laser radiation irradiation means of image output device shown in Fig. 9.
- [Fig.11]  
It shows a standard characteristic curve of the conventional color negative film.
- [Fig.12]  
It shows the characteristic curve shown using the density and transmittance.
- 30 [Fig.13]  
Explanation of the gradation of this invention.

[Explanation of signs]

35

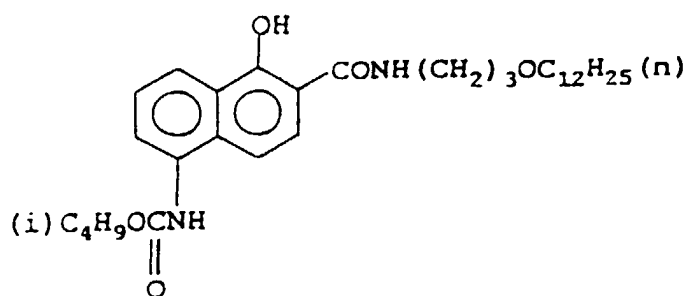
**[0315]** Explanation of signs in Fig. 1-10

- |       |   |
|-------|---|
| F     | film                                    |
| P     | color print or color paper              |
| 40 01 | DX code                                 |
| 03    | Development process                     |
| 04    | Manual development selection            |
| 1     | Image reading device                    |
| 5     | Image processing device                 |
| 45 8  | Image output device                     |
| 10    | Transmittance type image reading device |
| 11    | Light source                            |
| 12    | Quantity of light adjustment unit       |
| 13    | Color separation unit                   |
| 50 14 | Diffusion unit                          |
| 15    | CCD area sensor                         |
| 16    | Lens                                    |
| 17    | Amplifier                               |
| 18    | Analog to digital converter             |
| 55 19 | CCD correction means                    |
| 20    | Log converter                           |
| 21    | Interface                               |
| 22    | Carrier                                 |

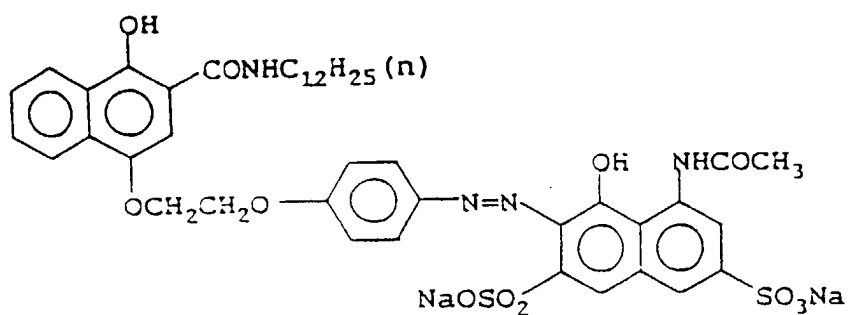
23	Motor
24	Driving roller
25	Frame detection sensor
26	CPU
5 48	Interface
49	Addition average operation means
50a	The first line buffer
50b	The second line buffer
51	The first frame memory unit
10 51R	R data memory
51G	G data memory
51B	B data memory
52	The second frame memory unit
52R	R data memory
15 52G	G data memory
52B	B data memory
53	The third frame memory unit
53R	R data memory
53G	G data memory
20 53B	B data memory
55	Selector
60	CPU
61	The first image processing means
62	The second image processing means
25 63	Input bus
64	Power output bus
65	Data bus
66	Memory
67	Hard disk
30 68	CRT
69	Keyboard
70	Communication port
75	Data synthesis means
76	Synthetic data memory
35 76R	R data memory
76G	G data memory
76B	B data memory
78	Interface
79	CPU
40 80	Image data memory
81	D/A converter
82	Laser radiation irradiation means
83	Modulator driving means
84a,b,c	Semiconductor laser source of light
45 85	Wavelength conversion means
86	Wavelength conversion means
87R,G,B	Optical modulator
88R,G,B	Reflection mirror
89	Polygon mirror
50 90	Color paper
91	Magazine
92	Punch means
94	Color development tank
95	Blix tank
55 96	Washing tank
97	Dryer part
98	Cutter
99	Sorter

- 100 Color concentration gradation conversion means
- 101 Saturation conversion means
- 102 Digital magnification conversion means
- 103 Frequency processing means
- 5 104 Dynamic range conversion means

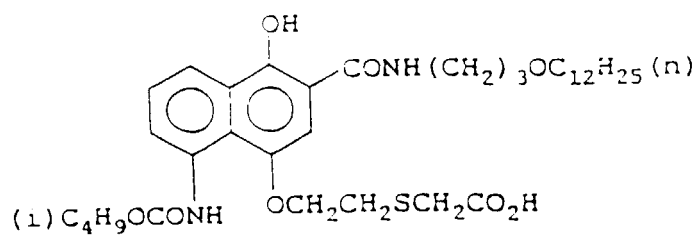
ExC-1



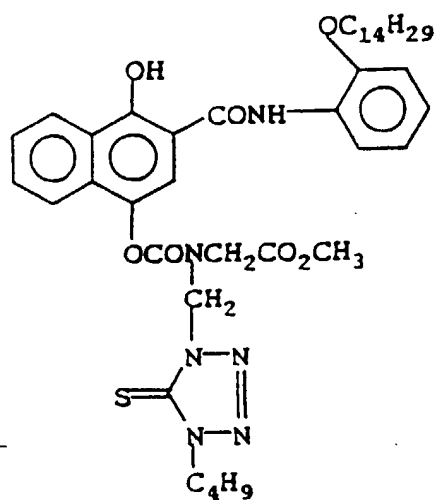
ExC-2



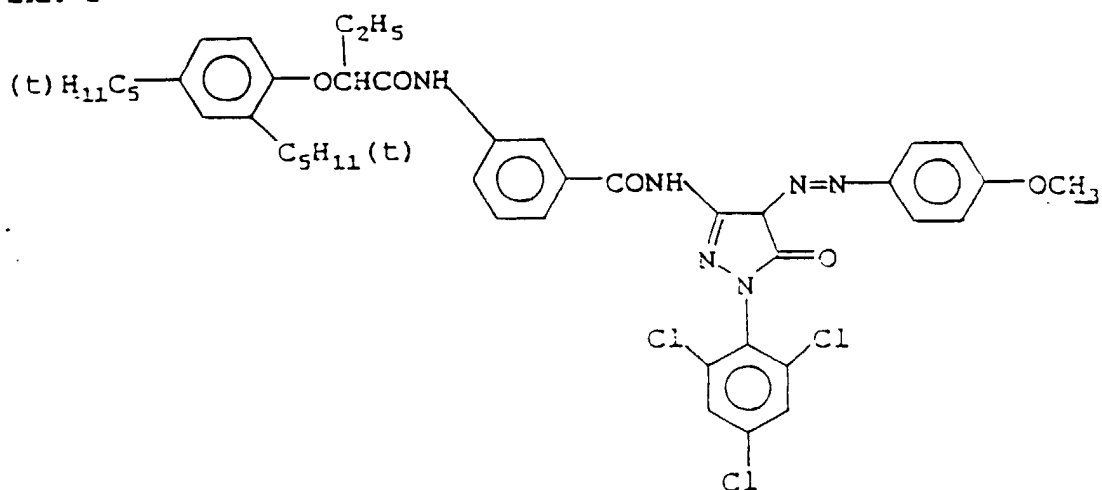
ExC-3



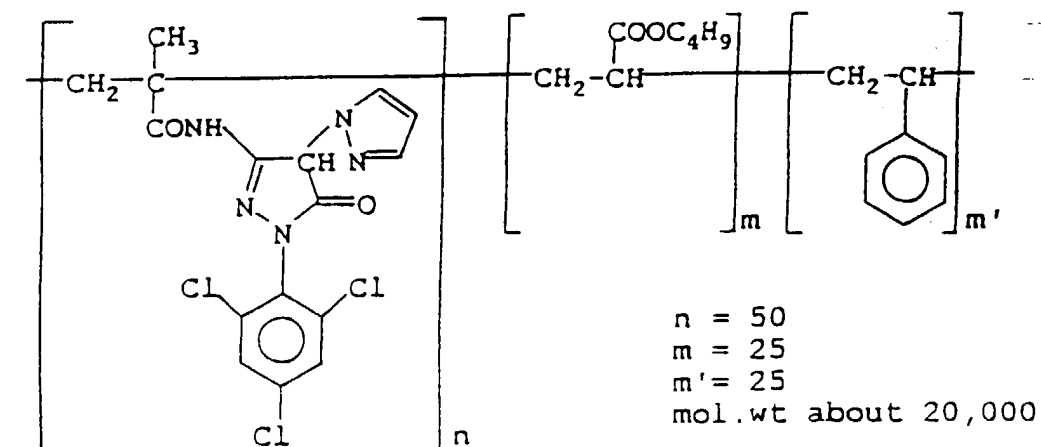




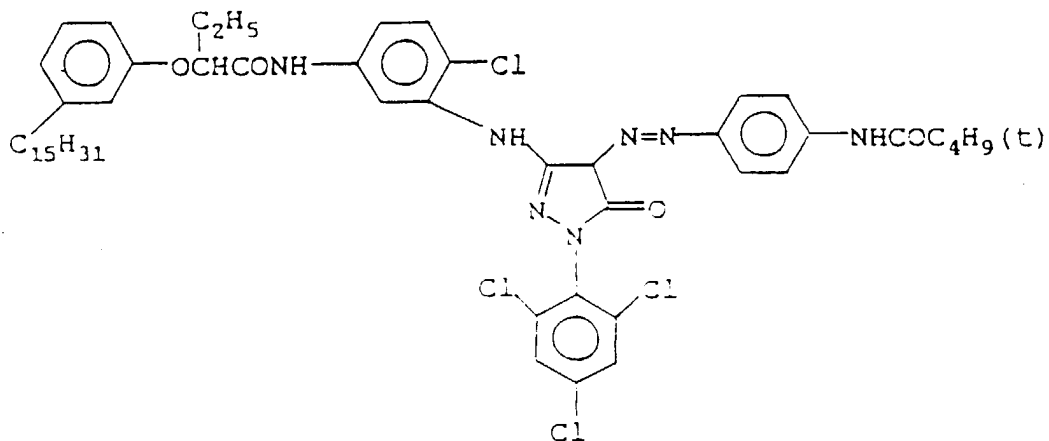
ExM-1



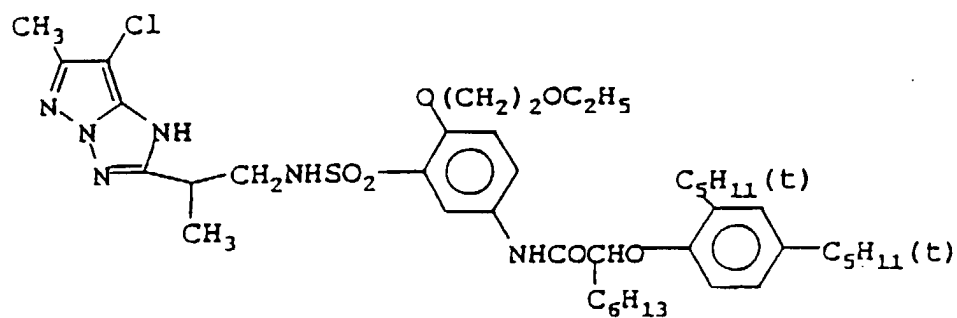
ExM-2



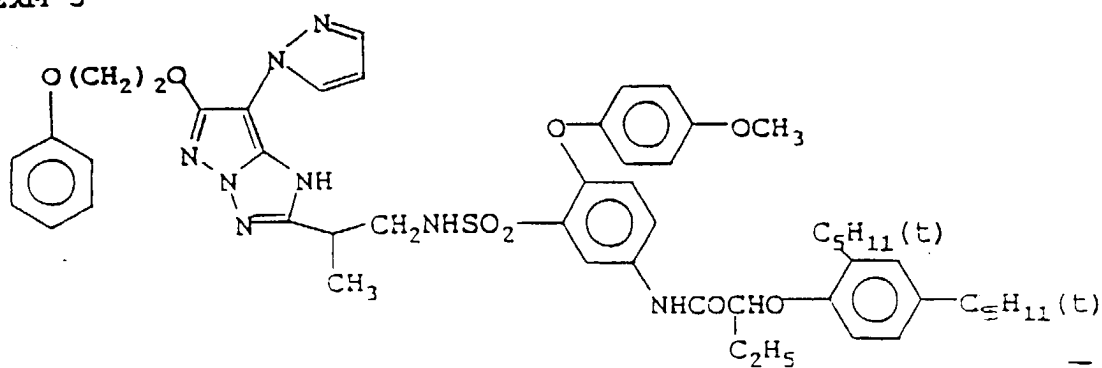
ExM-3



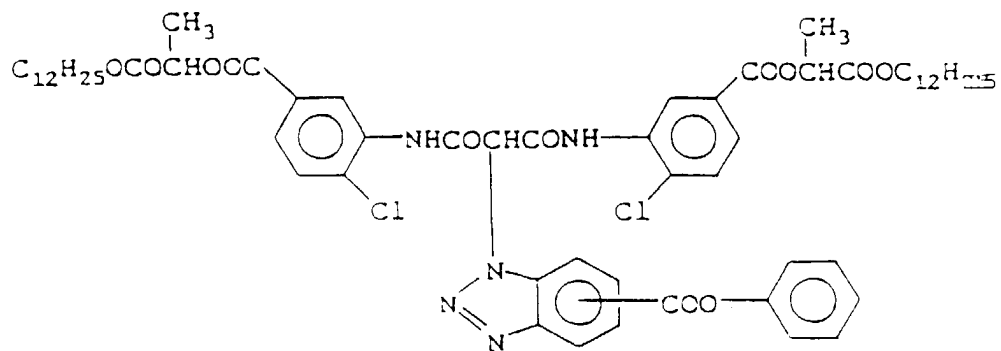
ExM-4



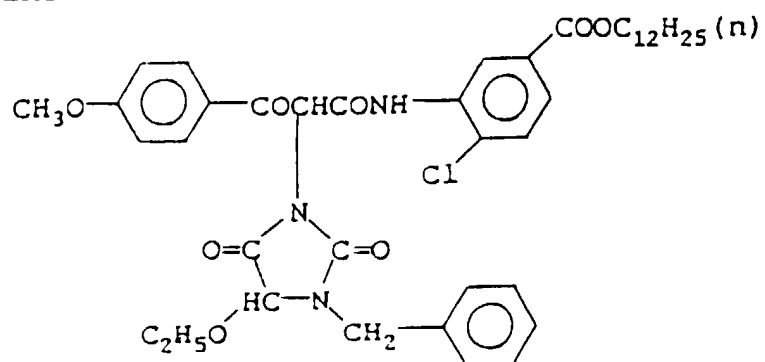
ExM-5



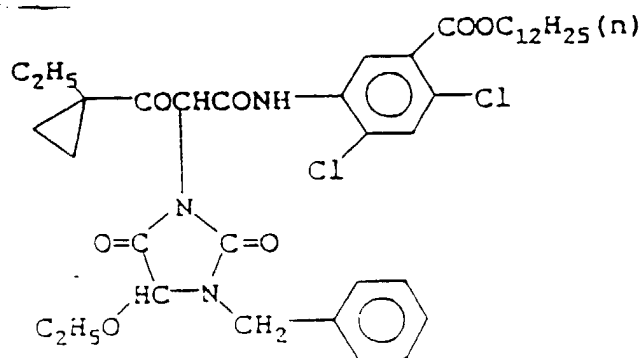
ExY-1



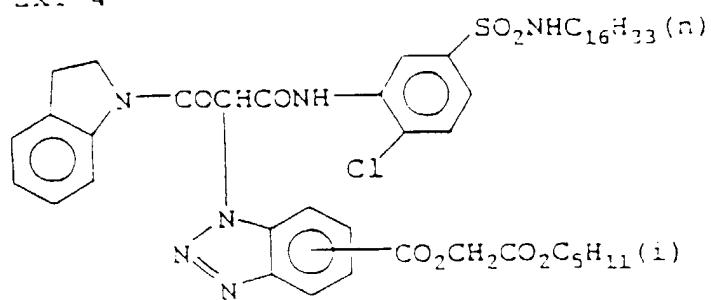
ExY-2



ExY-3

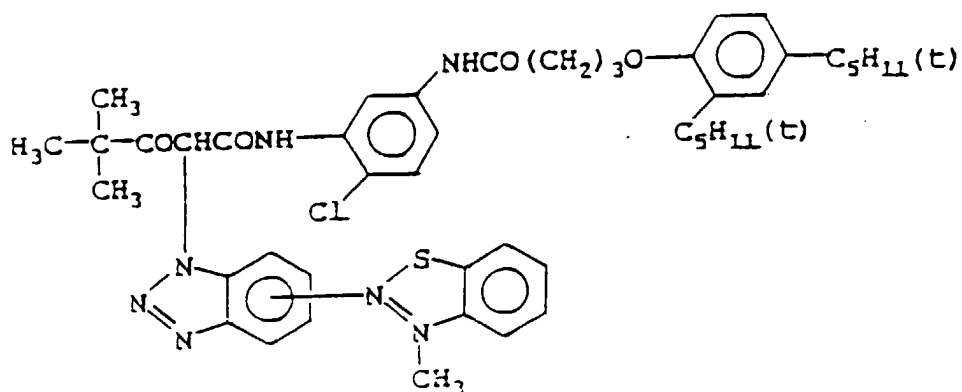
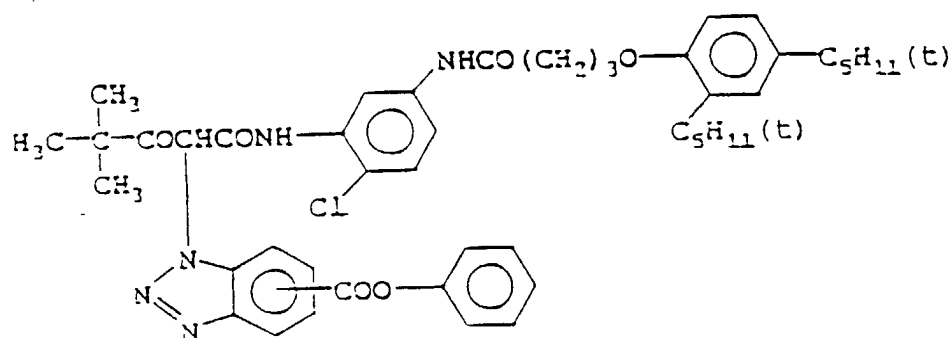


ExY-4

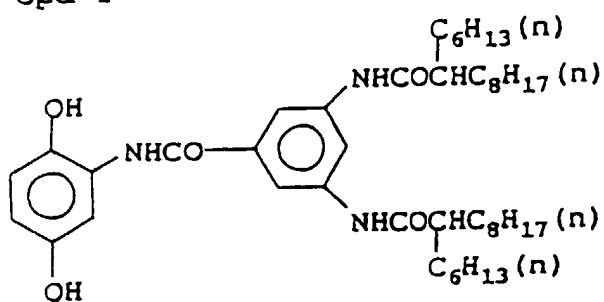




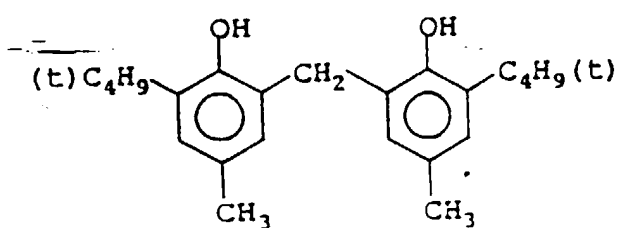
ExY-5

~~ExY-6~~

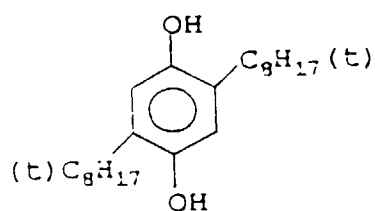
Cpd-1



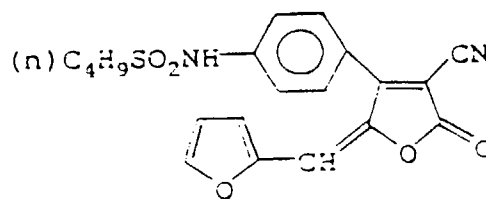
Cpd-2



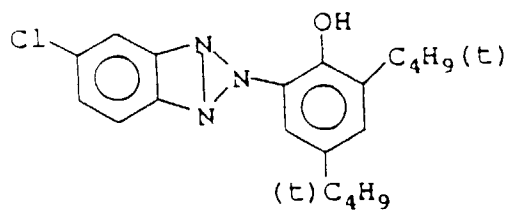
Cpd-3



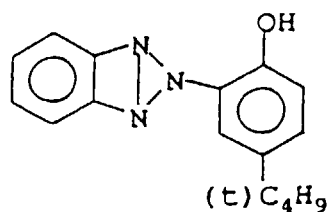
Cpd-4



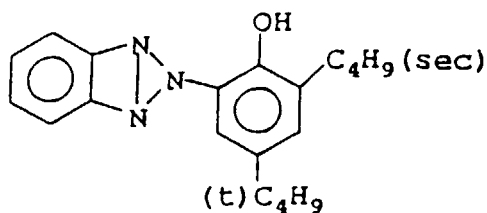
UV-1



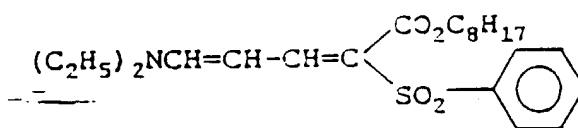
UV-2



UV-3

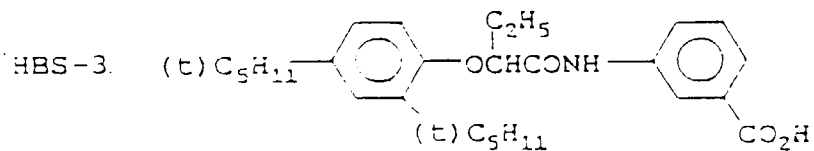


UV-4

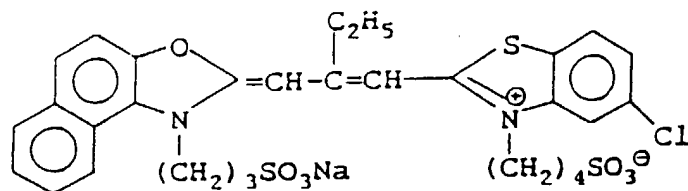


HBS-1 tricresylphosphate

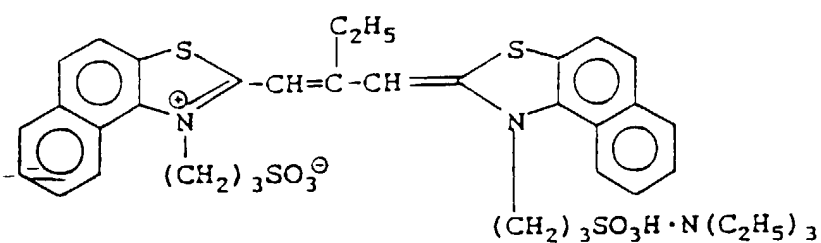
HBS-2 di-n-butylphthalate



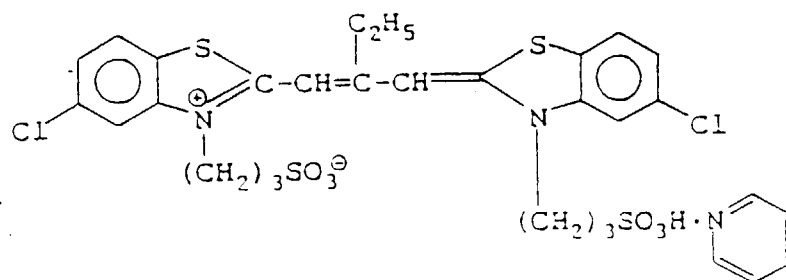
ExS-1



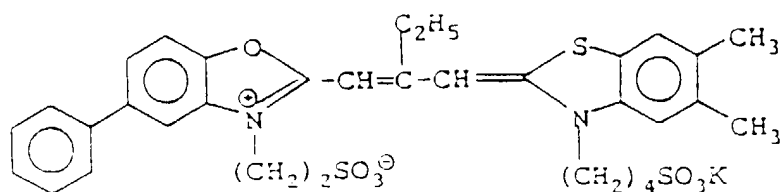
ExS-2



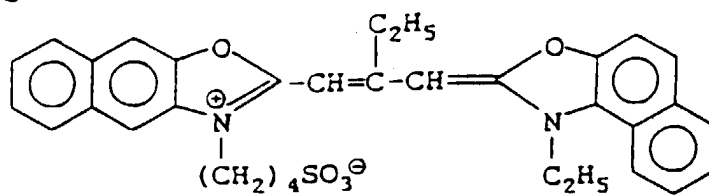
ExS-3



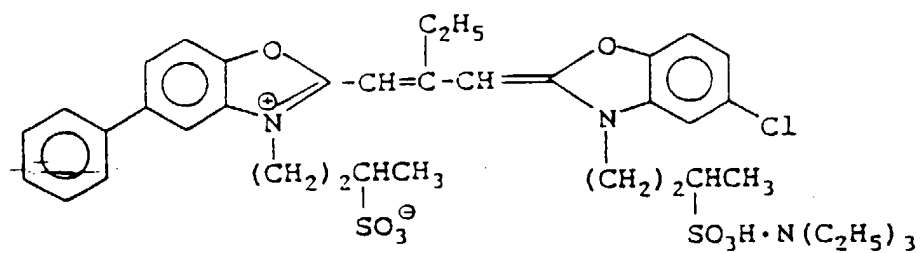
ExS-4



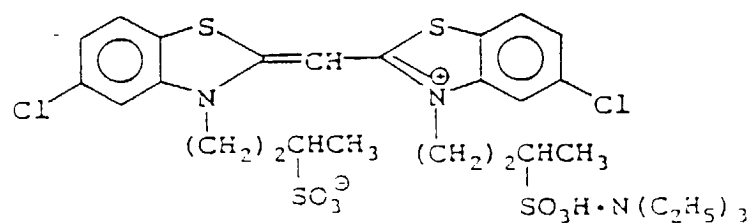
ExS-5



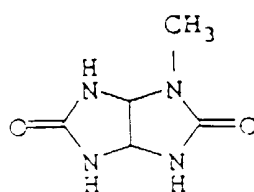
ExS-6



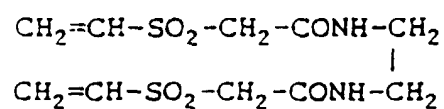
ExS-7



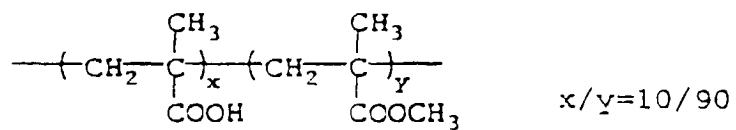
S-1



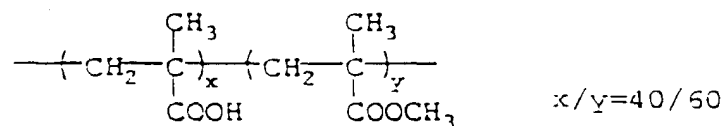
H-1



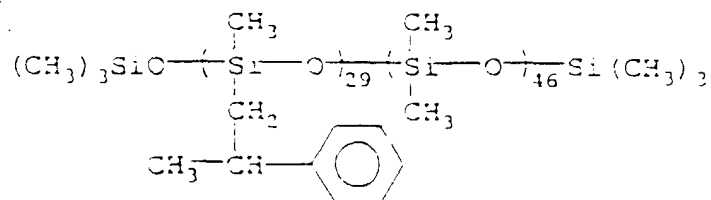
B-1



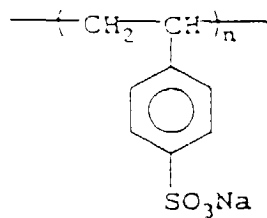
B-2



B-3

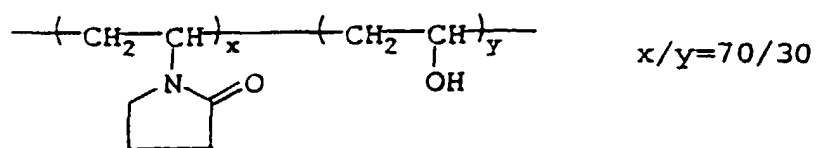


B-4

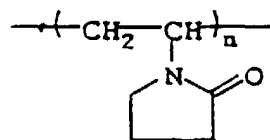


Average molecular weight: about 50,000

B-5

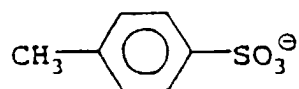
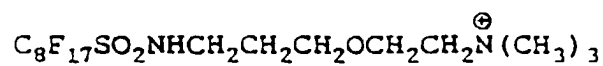


B-6

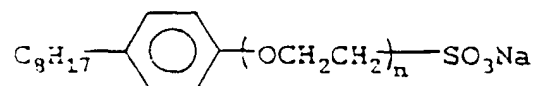


(mol. wt. about 10,000)

W-1

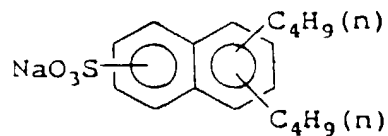


W-2

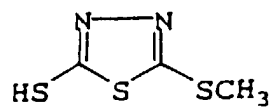


n = 2 to 4

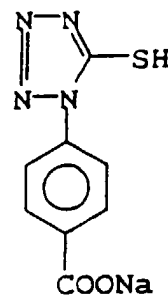
W-3



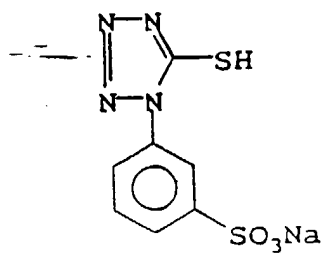
F-1



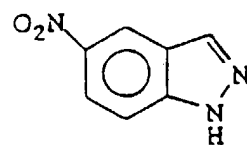
F-2



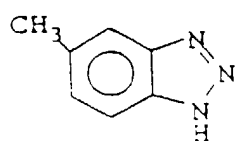
F-3



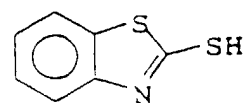
F-4



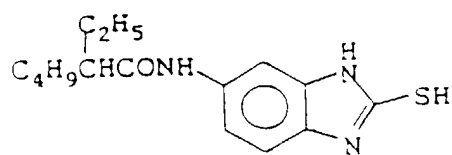
F-5



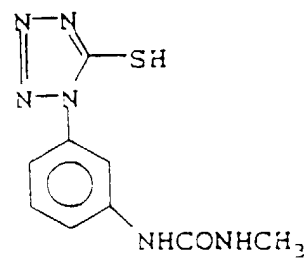
F-6



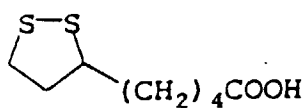
F-7



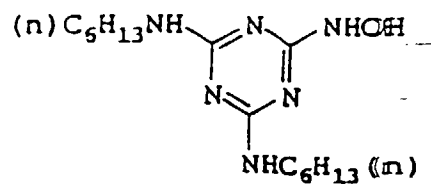
F-8



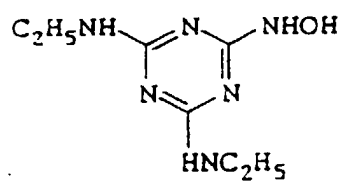
F-9



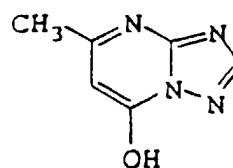
F-10



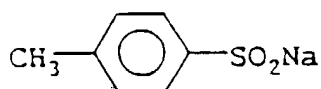
F-11



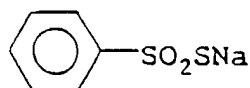
F-12



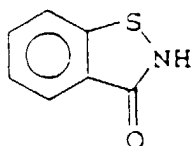
F-13



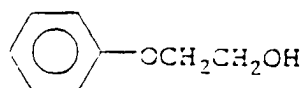
F-14



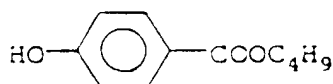
F-15



F-16



F-17



# Claims

1. An image forming process, said process including the development of an exposed color photographic material, which has blue light sensitive layer having yellow dye forming coupler, green light sensitive layer having magenta dye forming coupler, and red light sensitive layer having cyan dye forming coupler, and output of the image information to an output device, wherein said process comprises:
  - (1) photoelectric reading of the recorded image information on the said developed color photographic material,
  - (2) conversion of the image information obtained by said photoelectric reading into a digital image information,
  - (3) providing said digital image information with digital image processing so that preferable image characteristics can be obtained, and
  - (4) output said information on an output device, said color photographic material being characterized in that after development under standard conditions,
  - (5) for the yellow, magenta, and cyan colors the value of the minimum density,  $D_{min}$ , is 0.3 or less, and
  - (6) said color photographic material contains oil-in-water emulsions containing at least one dye forming coupler, at least one of the coupler containing layers has a coupler/oil ratio of 0.01 g/g or more and 0.30 g/g or less.
2. Process according to claim 1, wherein at least one of the coupler containing layers has a coupler/oil ratio of 0.01 g/g or more and 0.15 g/g or less.
3. Process according to claim 1 or 2, wherein said coupler containing layer is one of the highest sensitive layers of the red sensitive layers, or the green sensitive layers, or the blue sensitive layers.
4. Process according to claims 1 - 3, wherein said coupler containing layer is in the green sensitive layers
5. Process according to claims 1 - 4, wherein the output device is a computer monitor, a projector or a printer.
6. Process according to claim 5, wherein the image is output to a silver halide color photographic paper.
7. Process according to claims 1 - 6, wherein the thickness of said color photographic material is 22  $\mu m$  or less.



8. Process according to claims 1 - 7, wherein said color photographic material further is characterized in that after development under standard conditions, for the yellow, magenta, and cyan colors the value of  $T_1 - T_0$  is -0.15 or more, and 0.3 or less, said value being defined on the basis of the characteristic curve of the said color photographic material shown in a rectangular co-ordinate system, whose vertical axis shows the transmittance of the said developed photographic material and the horizontal axis shows the logarithm of the light exposure, the point A on the characteristic curve is defined at a transmittance of  $(T_{\max} - 0.03)$ ,

Ea is defined as the value of logarithm of the light exposure at the point A,  
the point B on the characteristics curve is defined at a transmittance of  $(T_{\min} + 0.03)$  ( $T_{\min}$  is the minimum transmittance),

Eb is defined as the value of logarithm of the light exposure at the point B,  
the transmittance value which corresponds to  $(E_a + E_b)/2$  on the straight line AB is defined as  $T_0$ ,  
and the transmittance value which corresponds to  $(E_a + E_b)/2$  on the said characteristic curve is defined as  $T_1$ .

9. Process according to claims 1 - 8, wherein the substrate of said color photographic material is polyethylene terephthalate, polyethylene naphthalate, or cellulose triacetate.

10. Color photographic material for picture taking for use in the process of claims 1 ~ 9, characterized in that after development under standard conditions, for the yellow, magenta, and cyan colors the value of the minimum density,  $D_{\min}$ , is 0.3 or less, and said color photographic material contains oil-in-water emulsions containing at least one dye forming coupler, at least one of the coupler containing layers having a coupler/oil ratio of 0.01g/g or more and 0.30g/g or less.

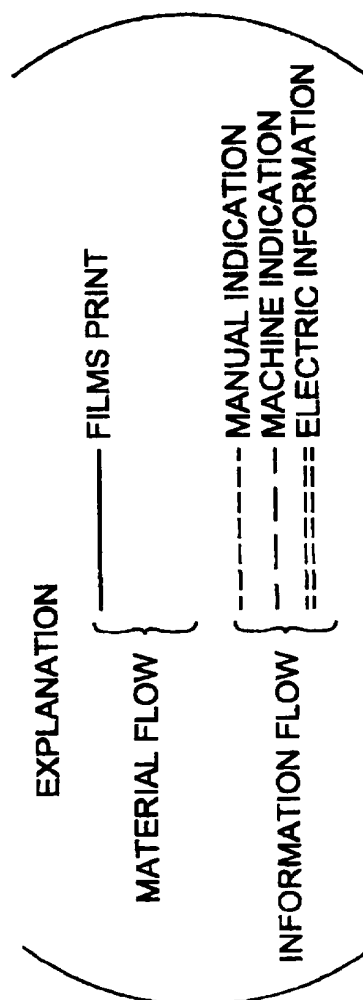
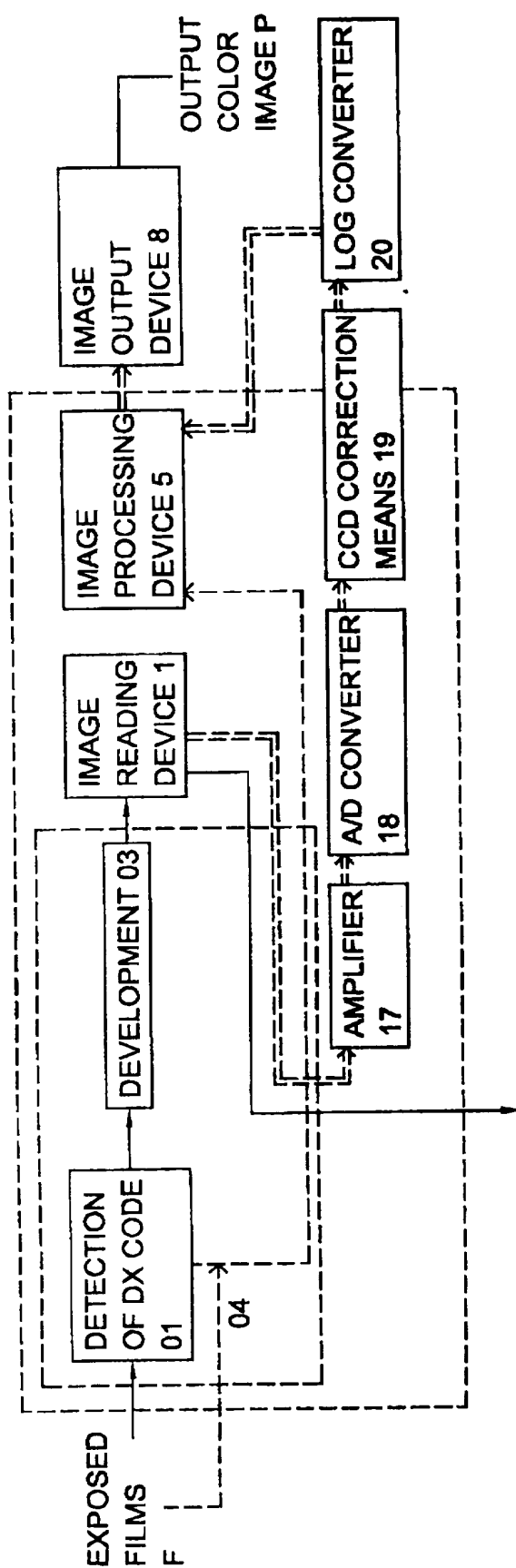


Fig. 1

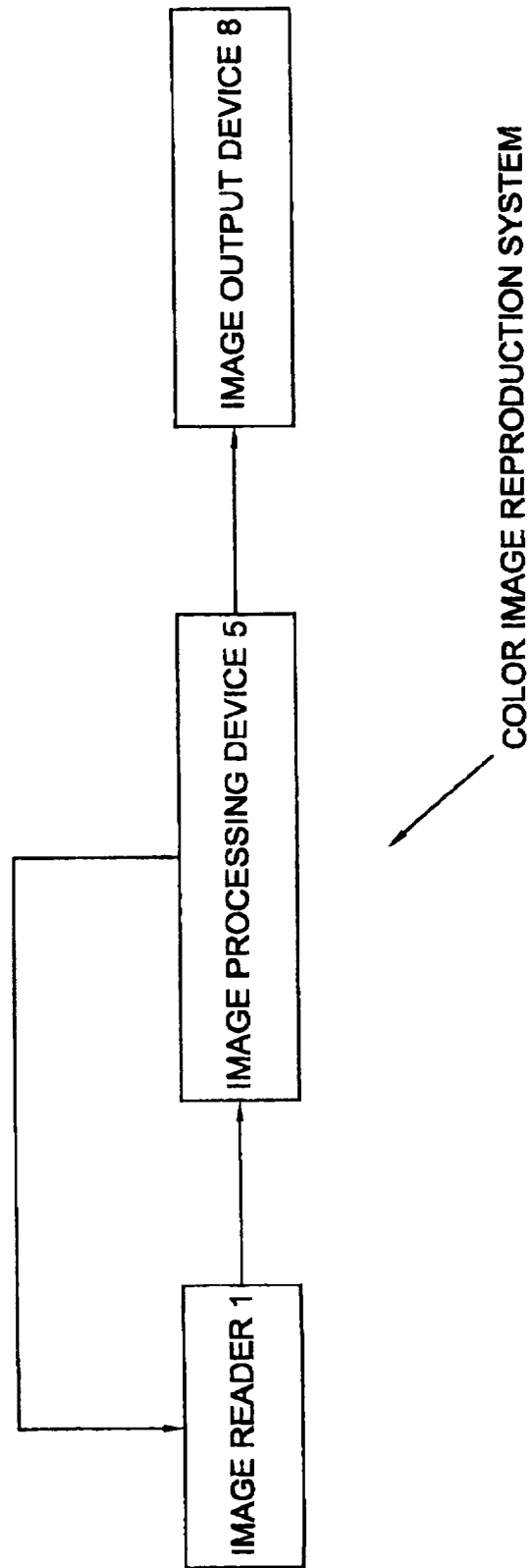


Fig. 2

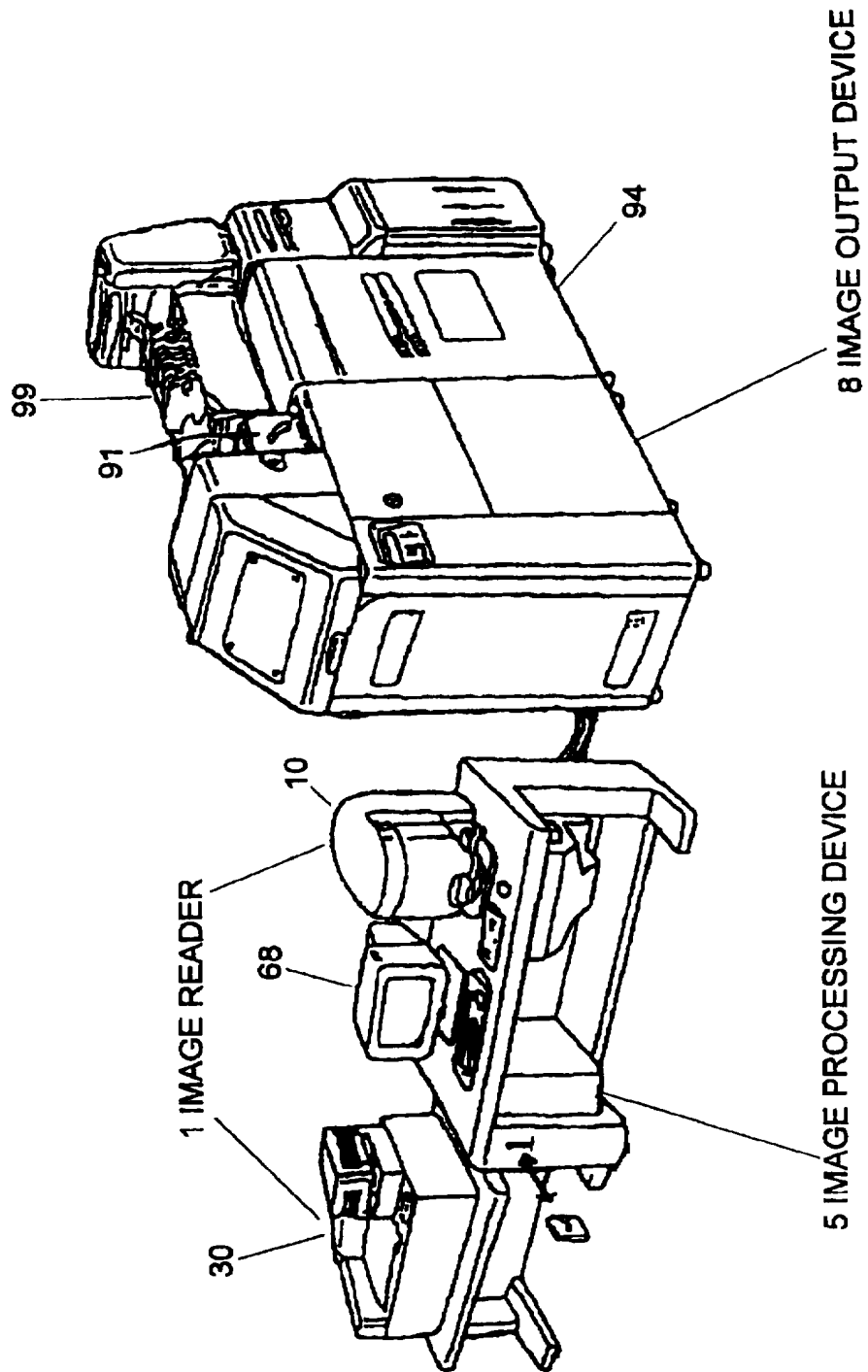


Fig. 3

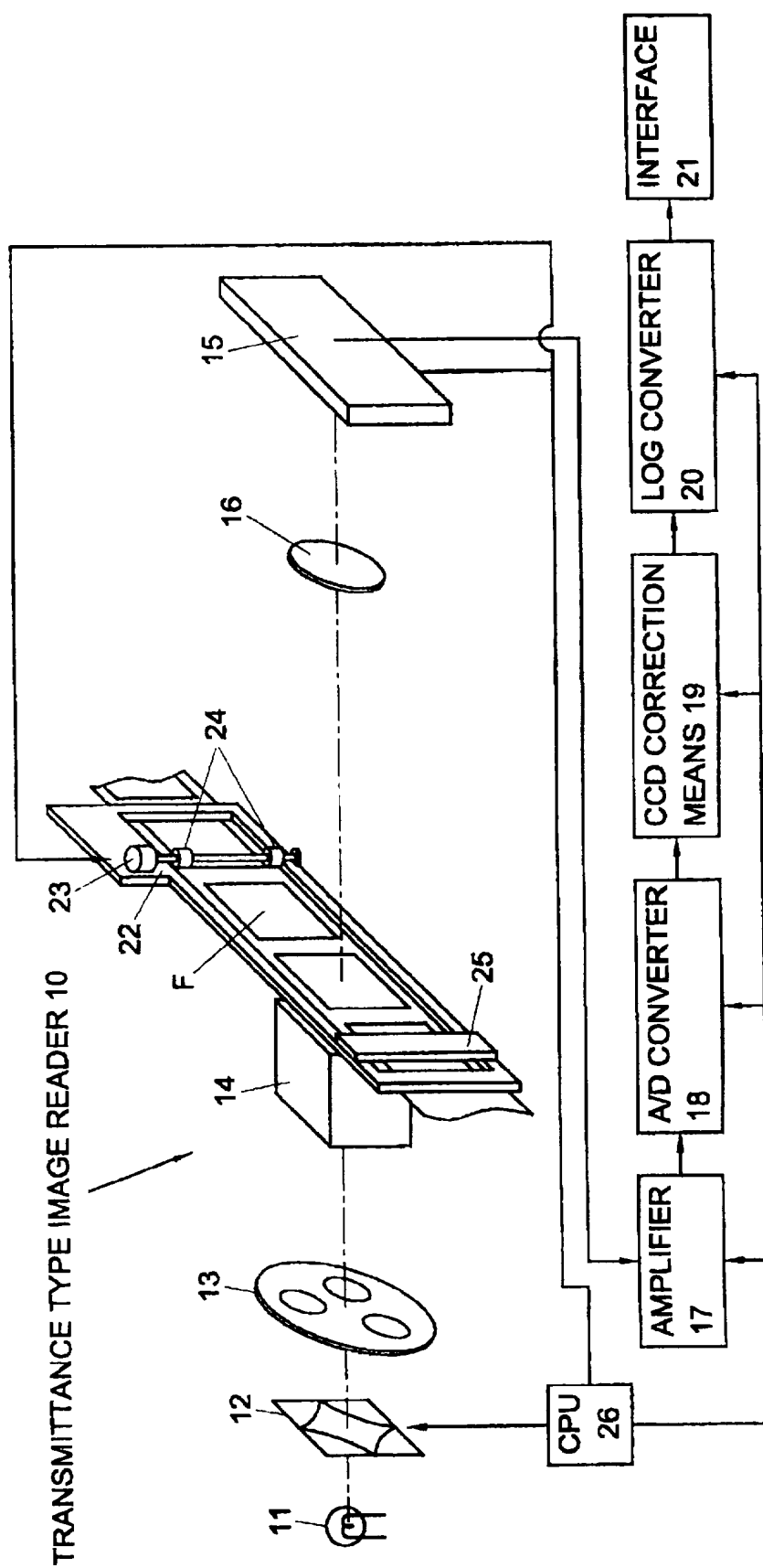
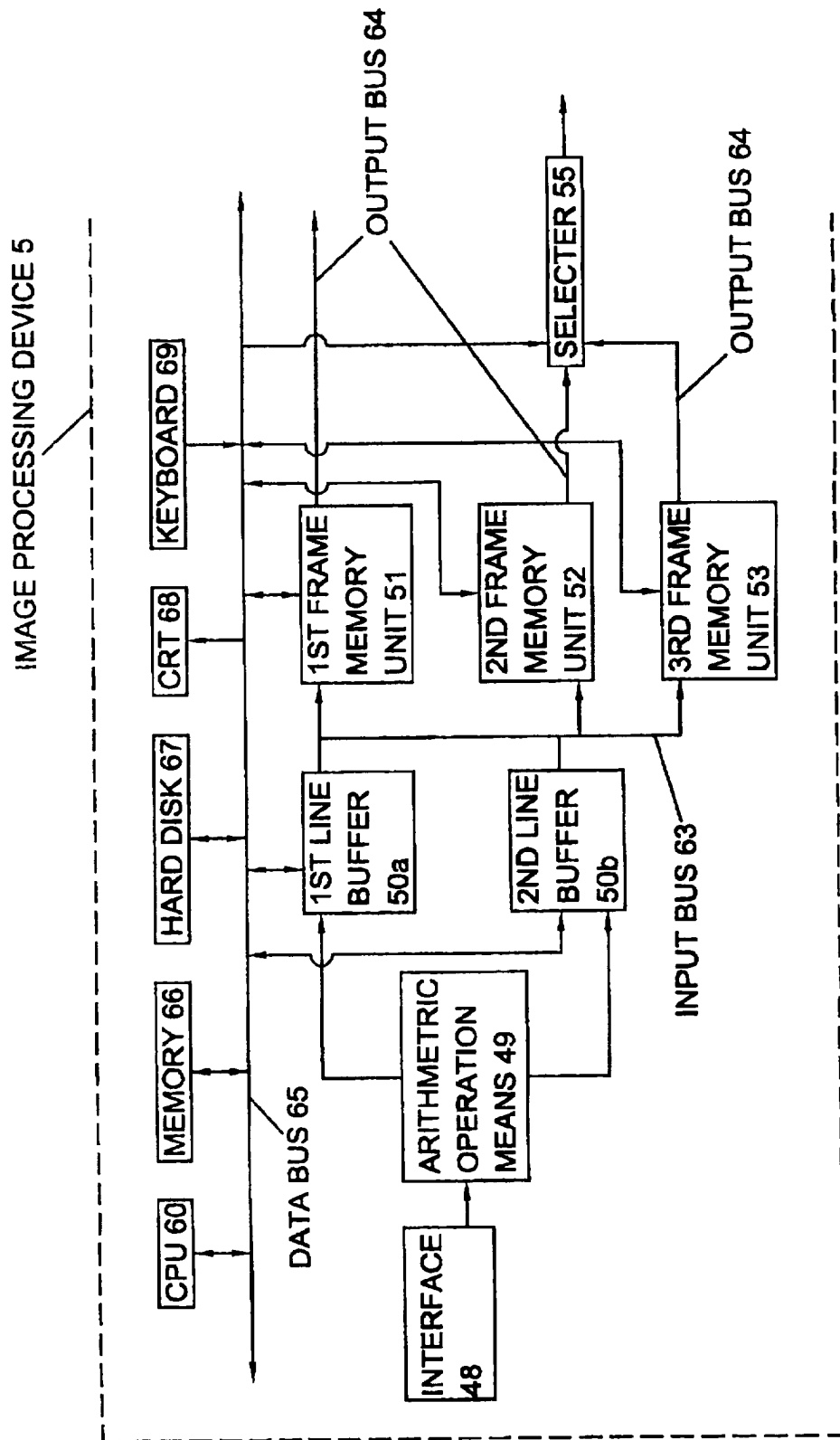


Fig. 4



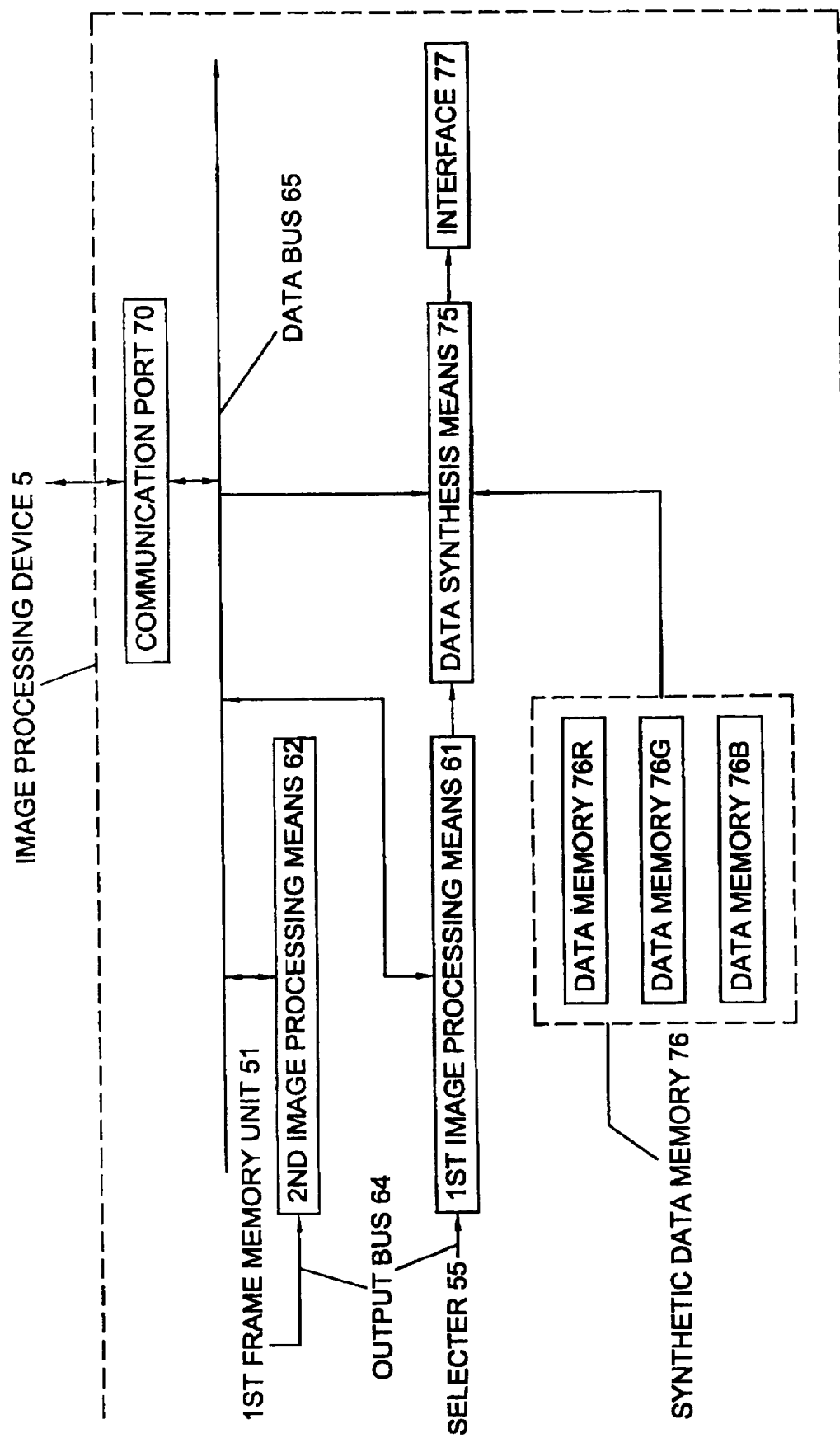


Fig. 6

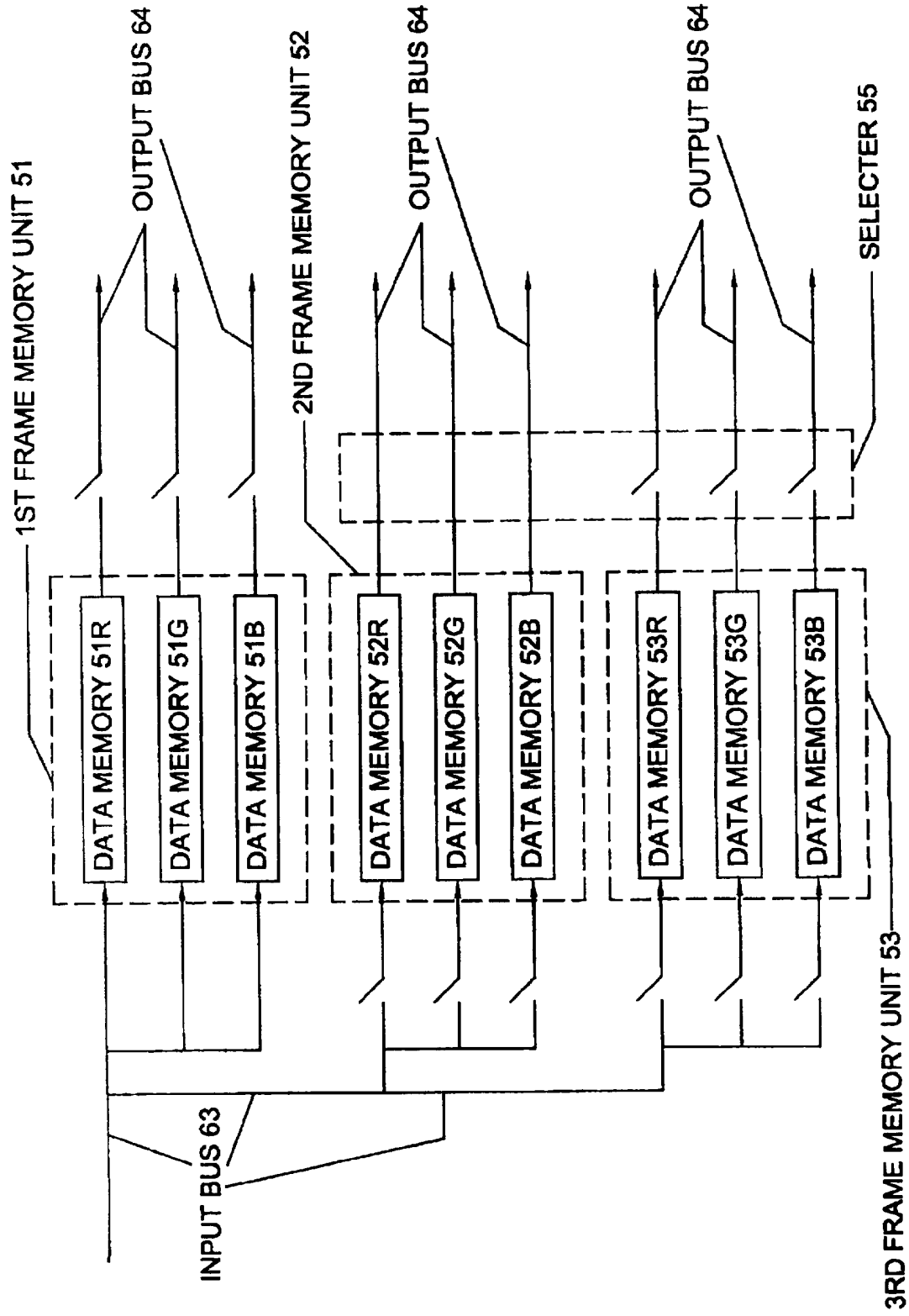


Fig. 7



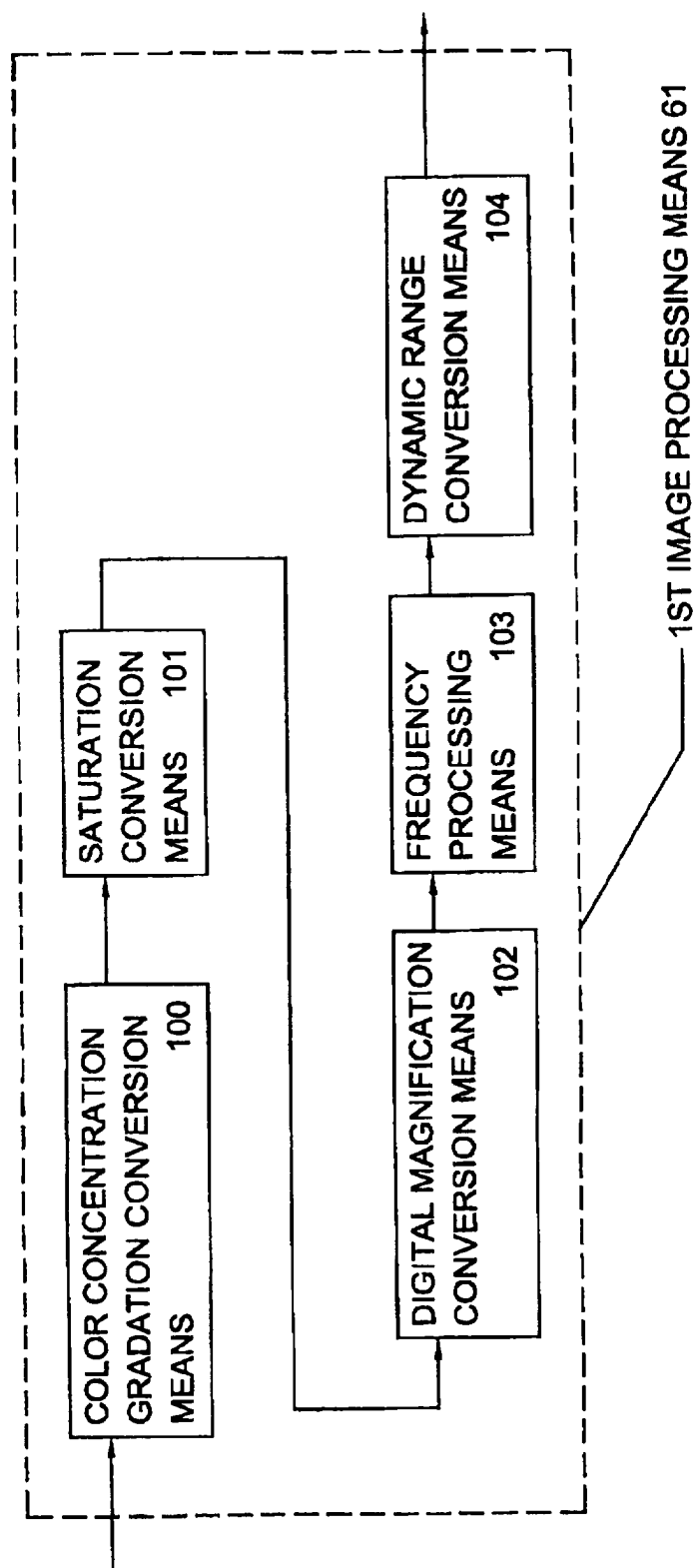
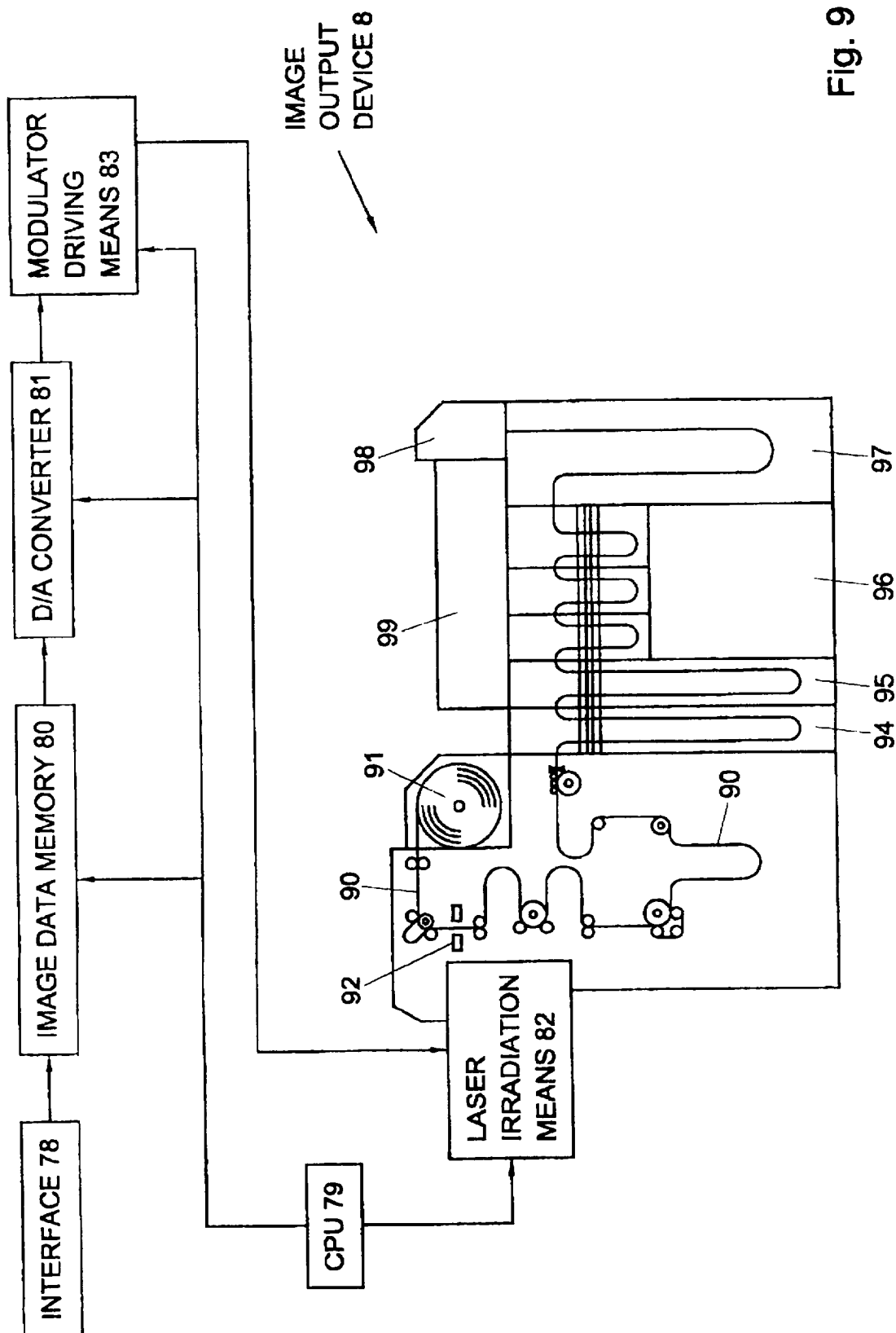


Fig. 8



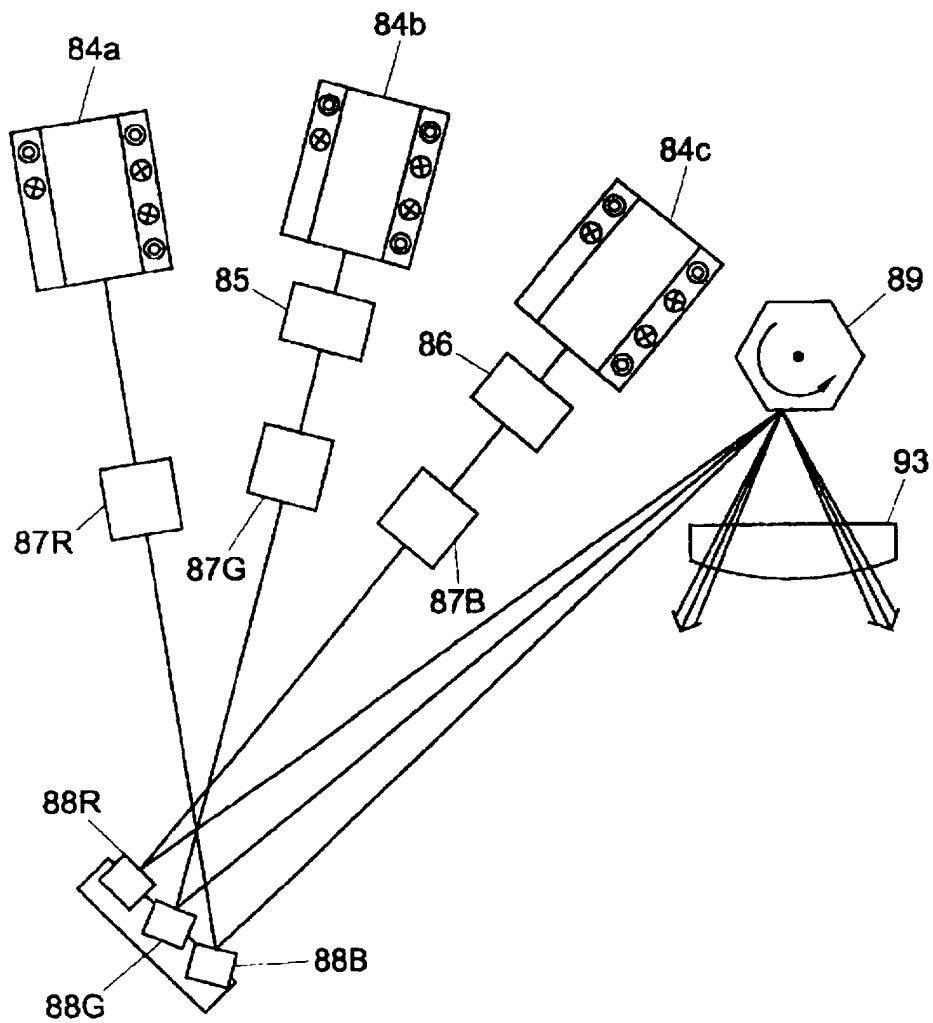


Fig. 10

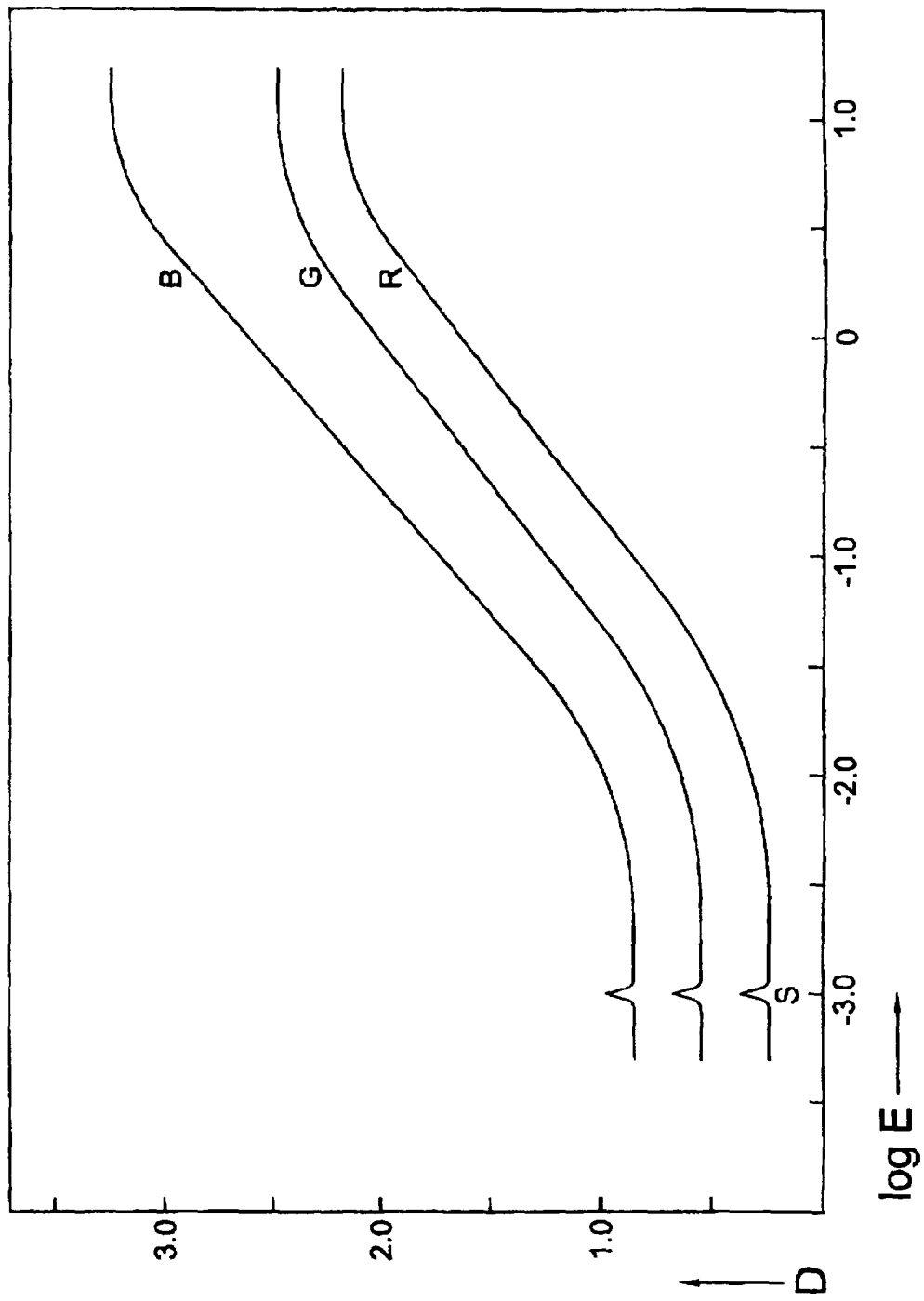


Fig. 11

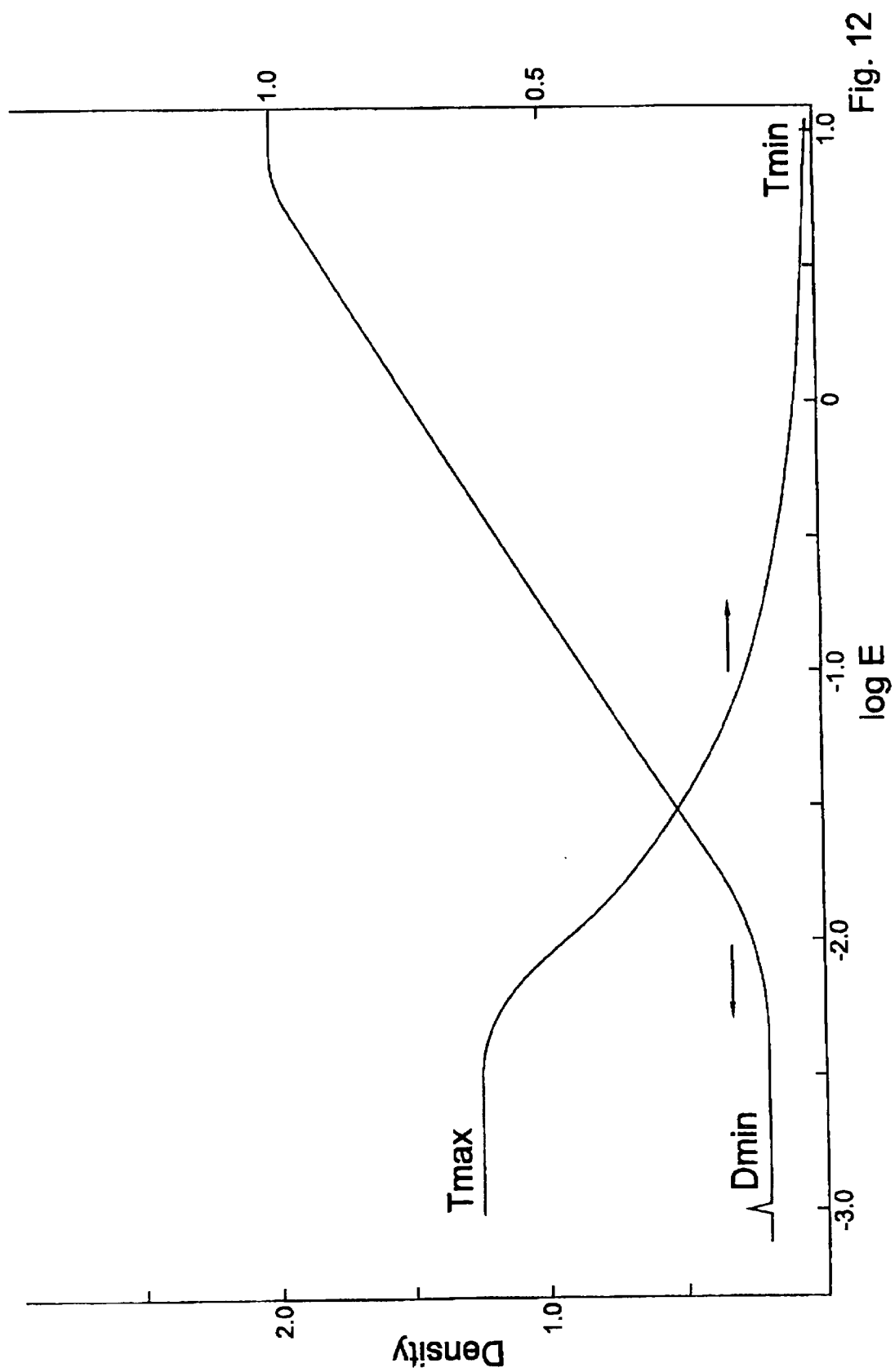


Fig. 12

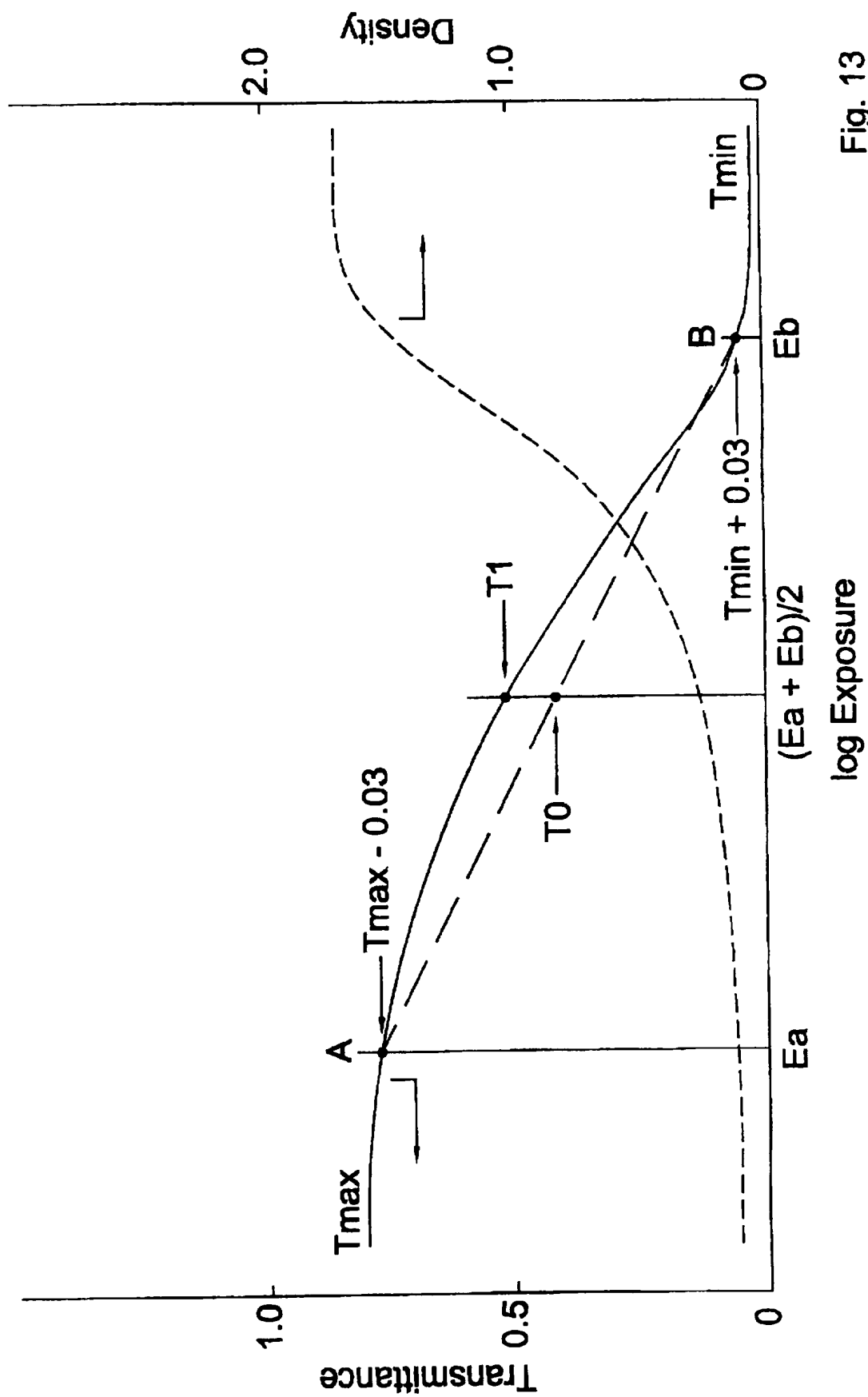


Fig. 13



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 99 20 2189

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.7)
A	EP 0 905 561 A (EASTMAN KODAK CO) 31 March 1999 (1999-03-31) * page 3, line 25 - line 35 * * claims 1,3,8-11; table 1 * ---	1-10	G03C7/30
A	US 5 837 433 A (SZAJEWSKI RICHARD P ET AL) 17 November 1998 (1998-11-17) * column 1, line 25 - column 6, line 44 * * claims 1-3,12,13 * ---	1-10	
A	US 5 389 504 A (LING HANS G ET AL) 14 February 1995 (1995-02-14) * column 1, line 34 - line 58 * * column 4, line 17 - line 29 * ---	1-10	
A	US 4 952 485 A (SHIBAHARA YOSHIHIKO ET AL) 28 August 1990 (1990-08-28) * column 87, line 11-14,21-23 * * column 97; table 2 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			G03C H04N
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>29 November 1999</b>	Examiner <b>Lindner, T</b>
CATEGORY OF CITED DOCUMENTS		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	
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			

EPO FORM 1503 03 82 (P44001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 20 2189

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-11-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0905561 A	31-03-1999	JP 11174637 A	02-07-1999
US 5837433 A	17-11-1998	US 5747228 A	05-05-1998
		GB 2324165 A	14-10-1998
US 5389504 A	14-02-1995	DE 69402469 D	15-05-1997
		DE 69402469 T	06-11-1997
		EP 0631181 A	28-12-1994
		JP 7168327 A	04-07-1995
US 4952485 A	28-08-1990	JP 6070711 B	07-09-1994
		JP 63226651 A	21-09-1988
		JP 6070710 B	07-09-1994
		JP 63226650 A	21-09-1988
		US 5091293 A	25-02-1992

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82