Oct. 15, 1940. B. H. CARROLL ET AL 2,218,229

PROCESS AND MATERIAL FOR MASKING IN COLOR CORRECTION

Filed March 31, 1937

Fig. 1.

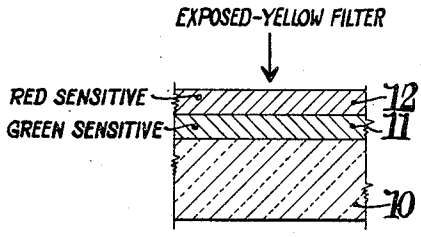


Fig. 2.

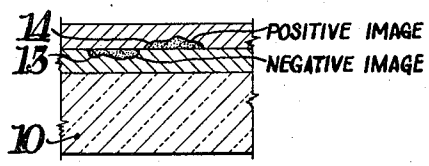


Fig. 3.

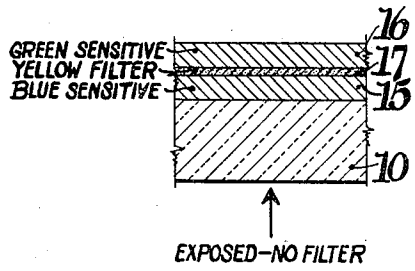


Fig. 4.

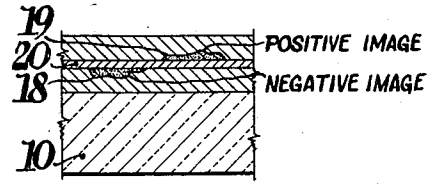


Fig. 5.

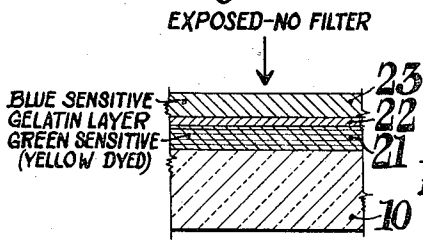
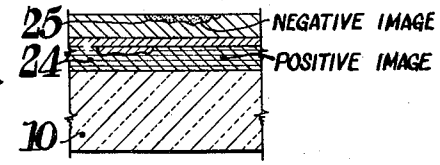


Fig. 6.



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PROCESS AND MATERIAL FOR MASKING IN COLOR CORRECTION

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1 Claim. (Cl. 95—2)

This invention relates to photographic reproduction and particularly to methods and materials useful in the graphic arts for reproduction of colored objects and natural colored scenes.

In the reproduction of colored objects and natural colored scenes pigments or inks are used which do not absorb and transmit light in the correct spectral regions. In order to overcome these deficiencies of the printing pigments or inks two general methods are in use. The first method involves a mechanical correction of the printing plates by means of hand retouching in order to render the result more nearly representative of the original subject. According to the second method of correcting for deficiencies in the pigments and inks, positive masks are used to print the corrected plates for certain of the color separations and a correction is thereby obtained photographically by a subtraction of photographic densities. In the masking method of color correction, it is necessary to secure exact registration of the masks with the corresponding negatives so that an accurate print can be made. A process of this type is described, for example, in a book entitled "The Modern Masking Method of Correct Color Reproduction" published by the Eastman Kodak Company, Rochester, New York in 1936. The necessity for registering the masks in this method of color correction has limited its utility.

It is, accordingly, an object of the present invention to provide a simpler masking method which obviates the necessity of registration of the masks. A further object is to provide an integral mask and a method of forming images therein.

These objects are accomplished by making use of a novel photographic element in which the sensitive layer designed to record the masking image is integral with the sensitive layer designed to record the color separation image. These layers are then processed by some means which produces a negative image of the color separation record and a positive image of the mask.

In the accompanying drawing,

Figs. 1, 3 and 5 are enlarged sectional views of photographic elements used according to our invention.

Figs. 2, 4 and 6 are enlarged sectional views of the corresponding elements after formation of images therein.

The essential feature of the masking process now in use is the printing of corrected positives by the use of masking positives placed in registry with one or more of the separation negatives during printing. The choice of the separation negatives which are to be corrected depends on the transmission and reflection characteristics of the printing inks. With inks available at present, it its generally desirable to correct the magenta and the yellow printing negatives, that is, the negatives made through the green and the blue filters, respectively. The blue-green negative made through the red filter usually does not need to be corrected. The general procedure is to correct the magenta printing negative with a mask which is a weak positive printed from the blue-green negative (made through the red filter), and to correct the yellow printing negative with a mask which is a weak positive made from the magenta negative (made through the green filter). However, a negative made by light corresponding to any of the three tri-color filters may be masked by a positive made by a light corresponding to either of the other two.

Our general procedure is to use a photographic plate or film provided with two layers of emulsion having different spectral sensitivities, one coated over the other so that the images formed in the two layers are permanently in register. The two layers may or may not be separated by a gelatin inter-layer. Such inter-layers at present may be dyed to act as filters or one of the layers of emulsion may be dyed. One of the emulsions will be developed to a normal negative, and the other emulsion will be converted to a positive by suitable means. The emulsion which is developed to a negative will be the more sensitive or will have higher contrast as the masking positive will always be weaker than the negative.

Various techniques may be employed in the processing of the sensitive element. One method of securing differential treatment of the layers is to employ means for controlling the diffusion of the processing baths, so that the action of the baths is limited to the outer sensitive layer. In this case, an emulsion layer which is to record the negative image is coated next to the support and an emulsion layer which is to record the positive image is coated over it. These emulsion layers may be separated by an inter-layer of gelatin although this is not absolutely essential. After exposure both emulsions are developed, but not fixed. After washing to remove the developer, the silver image in the upper layer is removed by

a suitable bleach bath, such as a mixture of quinone and hydrochloric acid in isopropyl alcohol containing small amounts of water. By controlling the time of action of bath and the concentration of water in the solution, it is possible to convert the image in the upper layer to silver chloride without affecting the lower layer. The silver chloride may then be removed by treatment with a sodium sulfite solution, which may be saturated with dissolved silver bromide to prevent attack on the unexposed silver bromide. The plate or film is then fogged and the upper layer only is developed by using a developer, the diffusion of which may be controlled, for example, by means similar to that used in the bleach bath. A developer of this type is, for example, a solution of 1:2:4-trihydroxybenzene, triethylamine and sodium sulfite in isopropyl alcohol containing a small amount of water. After development of the upper layer to a positive, followed by treatment in an acid stop bath, the plate may be fixed in the usual manner.

In an alternative method involving the use of means to control the penetration of the treating baths a silver chloride emulsion is used for the lower layer. A slow fine-grain silver bromide emulsion is coated over this with or without a gelatin interlayer. In this case, after development in the usual way, the upper layer is treated with the quinone and hydrochloric acid bleach bath described above to convert the image in the upper layer only, to silver chloride. The film is then treated with a sodium sulfite solution which removes not only the silver chloride formed in the upper layer by bleaching, but also the undeveloped silver chloride of the lower layer. After washing, the undeveloped silver bromide of the upper layer may then be developed to a positive by any standard developer.

A second method of forming a positive image in only one of the layers is by bleaching a uniformly colored gelatin layer in the immediate vicinity of a silver image. The layer which is to record the positive image is uniformly dyed with dye absorbing the light to be used in printing, for example, a yellow dye. After exposure both layers will be developed to negatives and the plate or film fixed and washed, it will be then treated with a suitable bleaching bath, such as an acid solution of thiourea. The dye will be bleached in contact with the silver image in the dyed layer and, by suitable choice of dye and silver concentrations in this layer, the decrease in density caused by bleaching of the dye may be made to exceed the density of the silver, so that an effective positive image results for printing.

A third method of obtaining a positive image in only one layer is to employ an emulsion for one of the layers which gives a positive by solarization. The sensitivity of such layers is relatively low, but may be sufficient to be combined with a low sensitivity printing material where it is desired to obtain a corrected negative from a colored positive original.

Our invention will now be described by particular reference to the accompanying drawing. The drawing illustrates in Figs. 1 to 4 methods of processing, involving the use of differential diffusion and in Figs. 5 and 6 a method involving the use of bleaching pre-colored layers.

As shown in Fig. 1, a support 10 of any suitable transparent material, such as glass or cellulose esters, is coated with a green sensitive emulsion layer 11 and a red-sensitive emulsion layer 12. A thin gelatin layer may be interposed in the sensitive layers, but this is not absolutely necessary. The emulsion from which the layer 11 is formed is an emulsion which gives the usual amount of contrast and which may be developed to a density range of slightly over one. The emulsion from which layer 12 is formed is of a type which gives low contrast and should give a density range of about 40% of that of the emulsion of layer 11.

The element is exposed to a colored object or a natural colored scene through a yellow filter which prevents action of blue light on the sensitive layers. The green component of the colored object or scene is recorded in layer 11 and the red component is recorded in layer 12. The plate or film is then developed by one of the control diffusion methods described above to form a negative image 13 in the lower layer and a positive image 14 in the upper layer, as shown in Fig. 2. The plate or film formed in this way may then be used to print a corrected positive which is used in preparing the magenta printing plate.

As shown in Fig. 3, an element may be used which comprises a transparent support 10 coated with a blue-sensitive layer 15 and a green-sensitive layer 16. A yellow filter layer 17 is interposed between layers 15 and 16. This element is exposed from the support side to the colored object or natural colored scene to record the blue component of the object or scene in emulsion layer 15 and the green component in emulsion layer 16. The filter layer 17 prevents blue light from affecting the layer 16. After development of the plate or film by one of the controlled diffusion methods described, a silver negative image 18 is formed in the lower layer and a silver positive image 19 in the upper layers. As shown at 20, the yellow dye or filter layer 17 is removed during the processing, with or without the use of a separate bath.

As shown in Fig. 5, the support 10 is coated with an emulsion layer 21 containing a yellow dye uniformly dispersed throughout the layer. Over this is coated a plain gelatin layer 22 followed by a blue-sensitive layer 23. The yellow dyed layer 21 is sensitive to green light. This element is exposed from the emulsion side without making use of a special filter to record the blue component of a colored object or scene in layer 23 and the green component of the object or scene in layer 21.

The plate or film is developed, fixed and washed and is then treated in a suitable bleaching bath, such as an acid solution of thiourea which bleaches the yellow dye of layer 21 at the points adjacent the silver image. As shown in Fig. 6, this leaves a positive dye image 24 in the lower layer and a negative silver image 25 in the upper layer. This element may be printed with blue light to give a corrected color separation positive.

The positives printed from the elements of Figs. 4 or 6 are used to make the yellow printing plate.

The following examples, which are by way of illustration only, indicate methods of forming the corrected elements according to our invention.

Example I

A plate or film is coated with a negative emulsion sensitized for green light with a dye, such as 2:1'-diethyl-3:4-benzthia-2'-cyanine bromide. Over this is coated a thin layer of gelatin, followed by a thin layer of a low contrast emulsion sensitized primarily to red light with a dye, such

as 2,2'-diethyloxadicarbocyanine iodide. The element is exposed through a yellow filter which absorbs blue light, then developed throughout and washed. The image in the upper layer is then bleached by controlled diffusion in a bleach path which may be of the following composition:

Glycerine	cubic centimeters	500
Isopropyl alcohol	do	1,000
Quinone	grams	5
HCl	cubic centimeters	50

Time of action of this bath is controlled so that only the upper layer of emulsion is bleached; its action is stopped at this point by the use of a stop bath, which may be of the following composition:

Sodium bisulfite	grams	30
Isopropyl alcohol	cubic centimeters	1,000
Glycerine	do	1,000
Water	do	1,000

After the stop bath, the plate is washed. The silver chloride which has formed by action of the bleach bath is removed by use of a sodium sulfite solution containing silver bromide to reduce its attack on the remaining silver bromide; the formula is, for example:

Sodium sulfite	grams	100
Silver bromide	do	2
Water	cubic centimeters	1,000

Following this, the plate is washed and preferably dried. The plate is then exposed to fog it uniformly. The upper layer only is then developed by controlled diffusion of a developer which may be of the following composition:

A.	Isopropyl alcohol	cubic centimeters	500
	Hydroxy hydroquinone	grams	4
	p-phenylene diamine	do	0.25
B.	Water	do	200
	Sodium sulfite	do	10
	Glycerine	cubic centimeters	300
C.	Triethyl amine	do	10

The components are added to make solutions A and B. B is poured into A and C is added immediately before using. The plate is then washed and finally fixed to remove the unexposed AgBr in the lower layer and washed in the usual manner. There is thus obtained a negative made by green light and a positive made by red light. By printing this combination simultaneously on a sensitive emulsion layer, a corrected positive suitable for making the magenta printing plate may be obtained.

Example II

A plate or film is coated with a silver chloride emulsion sensitized to green light. Over this is coated a thin gelatin layer followed by a relatively slow fine-grain silver bromide emulsion sensitized primarily to red light. This element is exposed through a yellow filter and developed in the ordinary way. The image in the upper layer is then bleached by controlled diffusion in a bleach bath of the formula given under Example I, followed by a stop bath as given under Example I. The bleach bath converts the silver image in the upper layer to silver chloride. The plate or film is then fixed with a solution of sodium sulfite and silver bromide of the composition given under Example I. This solution removes the silver chloride in both layers. The plate is then washed and the remaining silver bromide in the upper layer is developed to a positive image by any standard developer, such as the following:

Monomethyl-p-aminophenol sulfate	grams	1.0
Na_2SO_3	do	75.0
Hydroquinone	do	9.0
Na_2CO_3	do	25.0
KBr	do	5.0
Water to	cubic centimeters	1000.0

Example III

An unsensitized emulsion sensitive to blue and violet light only is coated on a plate or film support. Over this is coated a layer of gelatin containing a non-diffusing yellow dye, such as chrysophenine (Schultz Farbstofftabellen 7th edition, No. 726). Over this layer is coated a layer of green-sensitive, low-contrast emulsion. The combination is exposed through the support without a filter. After exposure, the lower layer is developed to a negative and the upper layer is reversed by controlled diffusion to a positive. After fixing, the yellow dye is removed by an appropriate bath, such as sodium hydrosulfite. A corrected negative is thereby obtained for making the yellow printing plate of any of the usual photo-mechanical printing processes.

Example IV

A plate or film is coated with an emulsion dyed yellow with a non-diffusing azo dye, such as chrysophenine and sensitive to green light. A plain gelatin layer is preferably coated over the yellow coated layer and this is followed by a layer of blue sensitive, but not especially sensitized, emulsion. After exposure from the emulsion side without a filter, the element is developed and fixed in the usual way. It is then treated with an acid solution of thiourea of the following composition:

Thiourea	grams	7.0
Sulfuric acid (93%)	cubic centimeters	0.5
Hydroquinone	grams	3.0
Chrome alum	do	5.0
Water	cubic centimeters	200.0

This solution bleaches the dye in the lower layer differentially where the silver image is present. The element may then be printed with blue light to form a corrected positive representing the yellow printing plate.

As an alternative method, the lower emulsion layer may be dyed with Vat Yellow R (du Pont) which is then bleached on processing by treatment in an alkaline sodium stannite solution of the following composition:

$SnCl_2$-$2H_2O$	grams	8
Water to	cubic centimeters	100

To this add NaOH solution, 100 g. per liter, 100 cc.

To this add 2.5 mg. anthraquinone in 10 cc. triethanolamine.

It is to be understood that other methods of procedure may be employed according to our invention and that the above examples are merely for the purposes of illustration. Our invention contemplates numerous modifications, not specifically referred to herein and it is to be taken as limited only by the scope of the appended claim.

What we claim is:

The method of making a corrected color component image in a photographic element having two superposed silver halide layers, one of which contains a dye uniformly dispersed therein, which comprises forming in the layer not containing the dye a negative metallic silver image representing

one of the primary color components of a colored object, forming in the layer containing the dye a negative metallic silver image representing another primary color component of the colored object, bleaching the dye in the region of the last-mentioned negative image to form a positive dye image serving as a masking image and printing through the two images simultaneously with light of a color substantially complementary to the color positive dye image to form a corrected color component image representing the color complementary to that represented by the negative image.

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