

[54] **MATERIAL AND A PROCESS FOR THE PRODUCTION OF COLOR CORRECTED REPRODUCTIONS**

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[58] Field of Search.....**96/6, 5, 23**

[56] **References Cited**

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ciples of Color Photography, 1953, John Wiley & Sons, Inc. pp. 389-403, 545, 575-576, 585, 590-597 and 606

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Attorney—Connolly and Hutz

[57] **ABSTRACT**

A process for the production of color duplicates from a multicolored original by a photographic color reversal process comprising the steps of producing a black and white masking image from the color original, registering the black and white masking image with the original, exposing a multilayered color photographic duplicating material through the combination of the color original and the black and white masking image, the said duplicating material comprising a red sensitive silver halide emulsion layer with a color coupler for the production of the cyan partial image, a green sensitive silver halide emulsion layer containing a color coupler for the production of the magenta partial image and a blue sensitive silver halide emulsion layer with a color coupler for the production of the yellow partial image and color reversal processing the exposed material to produce a color duplicate in true colors.

6 Claims, No Drawings

MATERIAL AND A PROCESS FOR THE PRODUCTION OF COLOR CORRECTED REPRODUCTIONS

The present invention relates to a process for the production of color corrected reproductions, in particular color duplicates, and to photographic materials for performing the process.

There is an increasing demand in practice for the production from a transparent color original of so-called duplicates which are completely identical to the original in all important image qualities and particularly the colors.

The method generally applied for this purposes is the color reversal process in which a contact copy, or an enlargement of the original, is copied on to a special multilayered color photographic material suitable for photographic reversal processing. This reversal copying material is available both on transparent supports, (reversal copying film), and on opaque supports, (reversal copying paper). In this method, one positive color image is produced directly from another positive color image without making an intermediate color negative image. All such so-called direct positive processes, e.g. the silver dye bleaching process which directly produce a color copy, in principle give the same result and will hereinafter be referred to by the term "color reversal process".

Since color reversal diapositives generally have a high density range, and the available reversal copying material also has a gamma, sometimes called contrast or gradation, value (the symbol for which is the Greek letter γ) beyond the nominally required value of 1.00, the original diapositive is, in these cases, provided with a black and white mask of negative gradation consisting of a silver image, before the copy is produced on the reversal copying film. This mask reduces the density range of the original image and is, therefore, also known as "contrast reducing mask" which means that this mask reduces the gradation of the grey tone values, and hence also the density range of the original between "white" and "black". Since such masks also affect the colors to an extent which cannot be controlled, the colors obtained in the color copy are more liable to change and are variable in character if the color original, or the reversal copying material or even the gradation of the mask or the color of the light to which the mask is exposed, are changed.

It is among the objects of the present invention to overcome these disadvantages and to provide a process for the production of duplicates in true colors by means of a black and white mask. We now have found a process for the production of color copies from a multicolored original by a photographic color reversal process, using an uncolored mask obtained from the color original which mask is registered with the original for copying, and in which process

a. at least one of the image dyes for the partial image produced by colorforming development in the copy-forming material has equal side absorptions in the spectral ranges of the main absorptions of the dyes for the other two partial images, and

b. the photographic material for the production of the uncolored mask consists of one or more silver halide emulsion layers, each of which is associated in such a manner with the copy-forming material containing the image dye with equal side absorption, that the spectral sensitivity of the emulsion layer is complementary to the main density of the particular image dye and its gamma value is numerically equal, but opposite in sign, to the side absorption of this image dye, based on the grey equivalent color density 1.

The present invention relates both to the properties of the photographic material for the production of the reversal color copy and to the properties of the black and white mask or the photographic material for the production of the mask, which properties are related to each other in a particular way characterized by the invention. The reversal copying material contains a blue sensitive silver halide emulsion layer with a color coupler which yields upon color-forming development the dye for the yellow partial image, a green sensitive silver halide

emulsion layer with a color coupler capable of reacting with the oxidation product of a color-forming developer to form a magenta dye, and a red sensitive silver halide emulsion layer with a color coupler which yields upon color-forming development the dye for the cyan partial image.

According to the present invention, the reversal copying material is characterized in that at least one of the dyes for the partial images produced upon color-forming development must have equally high side absorptions in the spectral range of the main absorptions of the dyes for the other two partial images. Side absorptions or subsidiary densities as distinct from main absorptions are to be understood as meaning the absorption of the particular dye in the two thirds of the spectrum in which the dye should be completely transparent if copies in true colors are to be produced. Thus, for example, for the magenta dye the side absorptions lie in the blue and red third of the visible spectrum, i.e. in the wavelength regions of from 400 to 500 millimicrons and from 600 to 700 millimicrons; the main absorption lies in the green third of the spectrum (from 500 to 600 millimicrons). The most complete effect is, of course, obtained in the process of the present invention when the dyes of all three partial images satisfy the conditions relating to the side absorptions, but the side absorptions need only be equal for each individual dye image and may have different magnitudes for the three dye images. The means for meeting this condition are known. The lower of the two side absorptions is increased by adding a suitable quantity of a dye component which has its main density there. This method has, however, certain disadvantages. Since the quantity of dye component added is very small compared with the quantity of dye component which has to be corrected, the unequal behavior in the coupling kinetic of the two components results in that the desired equality of the two side absorptions is not maintained for the whole density range of the main absorption of the dye. In practice densities of from 0 to about 2.5 occur which necessarily leads to a falsification of color in the color copy. Moreover, the addition of such small quantities of dye component is very critical, and minor deviations in quantity produce a comparatively pronounced effect.

These disadvantages can be obviated by mixing suitable quantities of two or more dye components which have the same main absorption (e.g. two or more cyan color couplers), but have different side absorptions to make the side absorptions substantially equal. In the case of a cyan partial image in which the side absorptions are required to be equal, a cyan color coupler component Cyan I is used, the side absorption of which in the green third of the spectrum is higher than in the blue third of the spectrum, and a cyan color coupler Cyan II is used in which the reverse holds true with respect to the side absorption, and these two couplers are mixed in such quantities that equally high side absorptions are obtained in the two side thirds of the spectrum. The following numerical example shows that this object can in fact be achieved.

	Side Absorption	
	in the blue	in the green
Cyan I	bl = 0.15	gl = 0.29
Cyan II	blI = 0.25	glI = 0.18

If c_I and c_{II} are the required concentrations of Cyan I and Cyan II which when mixed provide the same side absorptions, the following equation must hold true:

Side absorption in the blue third of the spectrum = $c_I \cdot 0.15 + c_{II} \cdot 0.25$
 Side absorption in the green third of the spectrum = $c_I \cdot 0.29 + c_{II} \cdot 0.18$
 whence $c_I/c_{II} = 1/2$.

This means that Cyan I should be mixed with Cyan II in the ratio of 1:2.

In the following it is assumed that each of the three image dyes yellow, magenta and cyan of the copy-forming reversal film meets the first condition of this invention, namely equal side absorptions. The side absorptions are equal to a , b and c for the yellow, magenta and cyan dye of the copy-forming

material if it has just been exposed and processed in such a way that it shows a neutral color (grey) of density 1.00 (standardized adjustment). It should be noted that the side absorptions are here not based on the main density of the particular image dye but on the grey density which can be subtractively mixed with the given three image dyes (grey equivalent color density). In other words, the values for a , b and c are numerically equal to the absolute values for the side absorptions of yellow, magenta and cyan image dye when these colors are adjusted to grey of density 1.

According to the present invention, the condition for the black and white masking film associated with this copy-forming material is as follows: Each image dye with equal side absorption must have associated with it a mask layer having a gradation or gamma value equal to that of the side absorption of the image dye, and with a spectral sensitivity complementary to the image dye. Under the above condition, therefore, the masking films consist of three light sensitive silver halide emulsion layers, one of which is only blue sensitive and must be developed to the gamma value γ_b , the second is only green sensitive and must be developed to the gamma value γ_g , and the third is only red sensitive and must be developed to the gamma value γ_r , and the gamma values γ_b , γ_g and γ_r are numerically equal to the side absorptions a , b and c referred to above. Moreover, the sensitivity of these three layers measured at the threshold must be equal if the mask film is exposed to unfiltered light, (so-called white light). Accurate adjustment to the source of light is, however, not necessary in the case of white light since the gamma values of the three individual layers are very flat and at the most equal to a few tenths. The total gradation γ_M of the masking films is $a + b + c$. This, only in the rarest cases, exceeds a value of 0.50 and it is particularly advantageous to choose image dyes with the lowest available side absorptions as will be shown later.

The density curves of the masking film need not ascend in a completely straight line. On the contrary, as is well known it is advantageous to let the density curves flatten off in the so-called upper part ("shoulder"), because the reproduction of the light portions in the color duplicate is then better than if the ascent of the curve is completely rectilinear. If desired, the reproduction of light can be improved by a light mask combined in a known manner with the mask according to the invention.

In practice, the invention can be simplified in various ways without impairing its essential effect.

Since the yellow dye only has very slight side absorptions which, even in conventional masking processes, are regarded as negligible and may, therefore, be put equal to 0 ($a = 0$), the masking film need only consist of two layers, namely the green sensitive silver halide emulsion layer of gradation b and the red sensitive silver halide emulsion layer of gradation c . A material of this type has been disclosed e.g. in U.S. Pat. No. 3,485,627 in which the exact composition and other features (arrangement of layers, lack of definition, built-in filter layer) have also been described. The composition of this two-layered masking film can be still further simplified by providing only one light sensitive layer of gradation $b + c$ which is only green and red sensitive, and the sensitivity ratio for green and red actinic light corresponds to the gradation ratio b and c of the corresponding two-layered material. A material of this type has been described, for example, in U.S. Pat. No. 3,291,602. It has been found in practice that this material, which has been simplified to a single light sensitive layer, enables almost the same satisfactory color reproduction to be obtained in the reversal copy as with the two-layered masking film. The use of black and white masks in the production of color images in combination with dye images, which have equal side absorptions, is already known but the present invention differs fundamentally from such known processes.

In this known process multicolored intermediate images are interposed between the original and the reproduction, for example a color negative is taken from the original and serves as an original for the production of the copy. In the known

process, this intermediate image contains image dyes with equal side absorptions which only have black and white masks of the corresponding gradation associated with them. Although this process eliminates the side absorptions of the image dye of the intermediate image, and hence its effect on the color reproduction in the copy, it does not eliminate the errors due to the dye images of the copy-forming material. In the prior art process, there is no association between the image dyes of the copy-forming material and the black and white partial masks, and, therefore, no optimum color reproduction is achieved.

The present invention is basically distinguished over the foregoing prior art since in the process of the present invention the partial masks are determined by the image dyes of the copy-forming film. However, the masks are produced from the original image (original diapositive) and, in contrast to the prior art, not from an intermediate image (since there is none), nor from the image which contains the image dyes with the pairwise equal side absorptions (since in the present invention this is the reversal copying material and, therefore, not an image). Completely unexpected and unpredictable advantages arise from these fundamental differences. Because of the association of the properties of the reversal copy-forming photographic material with those of the masking film, a copying system consisting of these two materials and the instructions for use can be brought on to the market without having to take into consideration the originals, i.e. the optical properties of the image dye of these originals. The origin and optical properties of these originals are of no significance, and instead of transparencies reflection copies can even be used as originals and reproduced or duplicated equally successfully by this system. Another advantage is that the entire system can be rendered more economical and mechanized in that both the mask, since it has to be developed to a predetermined gradation, and the reversal copy-forming material can be processed in automatic apparatus according to a prescribed process.

In addition to the above mentioned conditions for associating the masking with the reversal copy-forming film according to the present invention, there now enters a third condition for obtaining a gradation in the duplicate equal to that of the original image. Since the gradation or gamma value of the original image is lowered by the masking, the gradation of the reverse copying film (γ_p) must accordingly be steeper than 1.00. In other words, if γ_M (equal to $a + b + c$) is the total gradation of the mask, $1 - \gamma_M$ is the gradation of the original which is provided with the mask according to the present invention, then the gradation γ_p of the reversal copy-forming material must be $\gamma_p = 1 / (1 - \gamma_M)$ or $\gamma_p (-\gamma - \gamma_M) = 1.00$.

The greater the gamma value of the mask, i.e. the higher the side absorptions of the image dyes of the reverse copying film, therefore, the higher must be the gamma value of the reversal copy-forming material.

This condition, of course, only applies if the reproduction is to be of the same type as the original, i.e. if a color diapositive is to be produced as a duplicate of an original color diapositive or if a reflection copy duplicate is to be produced from a reflection copy original, but the condition does not apply if the reproduction is required to have a different type of density range from the original, e.g. if a color diapositive is to be produced as a copy of a reflection copy or the converse. If the gradation, or what amounts to the same the density range of the copy, is to differ from that of the original by the factor v , then the above equations assume the following form:

$$\gamma_p = (v / (1 - \gamma_M)) \quad \gamma_p (1 - \gamma_M) = v$$

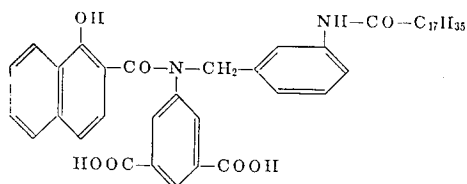
If a reflection copy is to be produced from a color diapositive by the process according to the present invention, then v is a number between 0 and 1 (proper fraction); in the reverse case, it is a number greater than 1. The copy-forming material must, therefore, have a gradation altered (reduced or increased) by this factor.

EXAMPLE 1

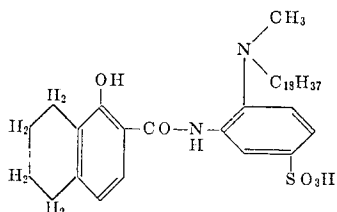
Copy-forming material

The following light sensitive layers are applied to a support of cellulose triacetate which has an antihalation layer:

1. A red sensitized silver bromide gelatine emulsion layer containing 2.8 g of silver bromide and 4 g of gelatine per square meter of dry layer which contains 0.72 g per square meter of the cyan coupler of the following formula (see U.S. Pat. No. 2,313,586):



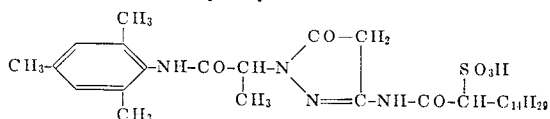
and 0.78 g. of the cyan coupler of the following formula (see German Pat. 1,137,311):



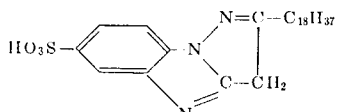
The first mentioned coupler has a side absorption, based on the main density in the red spectral region, of 4 percent in the blue and of 22 percent in the green region, and the second coupler mentioned has a side absorption of 15 percent in the blue region and 10 percent in the green region.

2. A protective gelatine layer containing 1.5 g of gelatine per square meter.

3. A green sensitive silver bromide gelatine emulsion layer which contains 2.8 g of gelatine, 2.0 g of silver bromide and 0.95 g and 0.15 g, respectively, of the two magenta couplers of the following formulas per square meter:



(See German Offenlegungsschrift 1,622,922)

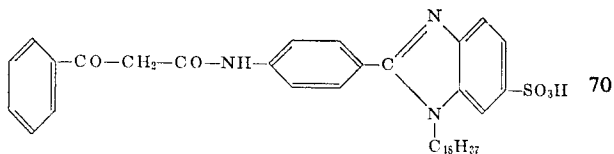


(See German Pat. 1,070,030)

Based on the green main density, these have a side absorption of 26 and 7 percent, respectively, in the blue region and of 15 and 12 percent, respectively, in the red spectral region.

4. A yellow filter layer which contains 1.5 g of gelatine and 0.3 g of colloiddally distributed silver per square meter.

5. A blue sensitive silver bromide gelatine emulsion layer containing 4.5 g of gelatine, 3 g of silver bromide and 1.5 g of the yellow coupler of the following formula:



(See German Pat. 900,781)

per square meter.

6. A protective gelatine layer containing 1.5 g of gelatine per square meter is arranged uppermost.

The copy-forming material has a gradation of 1.33 measured between the densities 0.7 and 2.0 after it has been processed. The side absorptions of the image dyes are 13 percent both for magenta and for cyan. For yellow, they are regarded as negligible.

Masking material

Calculation of the mask gradations:

The side absorptions of the image dyes in the copy-forming material are 0.13 for magenta and 0.13 for cyan, based on the main density in each case.

From this it is calculated that a colorless copy can be obtained from these image dyes composed of $0.76 \times$ yellow, $0.88 \times$ magenta and $0.88 \times$ cyan, which can be expressed in the following matrix scheme:

Yellow	Magenta	Cyan	
0.76	0.12	0.12	total = 1.00
0.00	0.88	0.12	total = 1.00
0.00	0.12	0.88	total = 1.00

The side absorptions a , b , c based on the side absorption 1.00 can be read off directly from this as $a = 0.0$, $b = 0.12$ and $c = 0.12$.

Composition of the masking material

An Isopan fine grain color emulsion (see BIOS Final Report, No. 1355, page 35) diluted 1 : 1 by the addition of a 3 percent aqueous gelatine solution is cast on a transparent polyester support based on polyethylene terephthalate of thickness 0.15 mm to produce a film 3.5 μ in thickness. In addition to the usual additives (hardeners, wetting agents) 40 mg of the red sensitizer Rr 1953 (see FIAT Final Report, 943, pg. 53) and 4 g of Acilanorange GX (Color Index No. 16230) in aqueous solution are added to the emulsion per kilogram of original emulsion.

A second layer of the above dilute Isopan fine grain color emulsion to which the green sensitizer Rr 340 (see FIAT Final Report, 943, pg. 46) and the same quantity of Acilanorange have been added before dilution is cast on this emulsion layer, again in a thickness of 3.5 μ . The quantity of sensitizer is such that these emulsions have the same sensitivity when they are exposed as a combination of layers through the antihalation layer (see below), and then developed for 2½ minutes in the developer described below. A hardened gelatine layer 1 μ in thickness is then cast on the uppermost emulsion layer for protection against mechanical damage. A 3 μ thick colored, clear, hardened antihalation layer containing one each of the known yellow, red and green dyes which can be bleached in photographic baths is applied on gelatine to the other side of the support. The color density of this layer is 1.5 behind a blue filter (Agfa-Gevaert Repro color separation filter 4); 0.3 behind a green filter (Agfa-Gevaert Repro color separation filter 5) and 0.3 behind a red filter (Agfa-Gevaert Repro color separation filter 622).

Preparation of the mask

The above described masked film is brought, with the colored antihalation layer, into contact with the transparent multicolored original which has to be masked and is exposed through this layer with unfiltered light. It was then treated for 2½ minutes in the following developer:

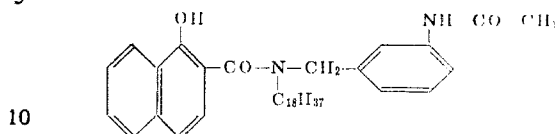
p-methylaminophenolsulfate	7.5 g.
Sodium sulfite	40.0 g.
Hydroquinone	3.5 g.
Soda (sicc)	30.0 g.
Potassium bromide	3.0 g.
Made up to 1 liter with water	

1 part of the resulting solution was diluted with 1 part of water.

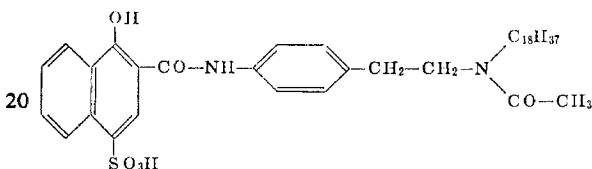
Development is continued until a total γ -value of 0.24 is reached. The film is then fixed in one of the usual acid sodium thiosulfate fixing baths and then washed and dried.

Oc1ccc2ccccc2c1C(=O)Nc3ccc(Cl)cc3S(=O)(=O)Nc4ccc(OCC)cc4

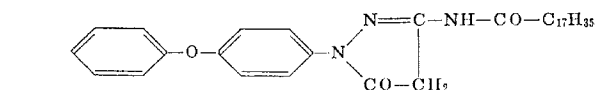
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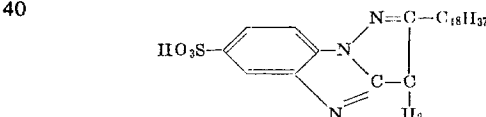


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75 2. The process of claim 1, wherein the photographic material for the production of the black and white mask contains a

mixture of two silver halide emulsions in form of a single silver halide emulsion layer, wherein the spectral sensitivity of one of these emulsions is complementary to the main absorption of one dye image and the spectral sensitivity of the other of these emulsions is complementary to the main absorption of another dye image of the copy-forming material which is to be corrected and the sensitivity ratio of the two emulsions corresponds to the gradation ratio of the side densities.

3. The process of claim 1, wherein the magenta partial image and the cyan partial image each have equal side absorptions.

4. The process of claim 1, wherein the gradation of the copy-forming material (γ_D) is related to the gradation of the mask (γ_M) as $\gamma_D(1-\gamma_M)=1$.

5. The process of claim 1, wherein at least one of the silver halide emulsions forming the cyan or magenta partial image contains a mixture of color couplers, each coupler of a mixture providing essentially the same main absorptions but

unequal side absorptions, and the color couplers are mixed in such a ratio that the sum of the side absorption provided by the color coupler mixture is substantially equal in the two thirds of the spectrum outside the main absorption.

6. A copy-forming material for performing the process of claim 1, comprising a red sensitive silver halide emulsion layer which contains at least one color coupler for the cyan partial image, a green sensitive silver halide emulsion layer which contains at least one color coupler for the magenta partial image, and a blue sensitive silver halide emulsion layer which contains at least one color coupler for the yellow partial image, wherein in at least one of the layers there is a mixture of color couplers each coupler in the mixture providing unequal side absorptions but these inequalities substantially compensating each other in the mixture so that the image dye produced upon color reversal processing has equal side densities.

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