

April 17, 1973

H. K. ZORN ET AL

3,728,121

MULTILAYER COLOR PHOTOGRAPHIC MATERIAL

Filed Aug. 19, 1970

3 Sheets-Sheet 1

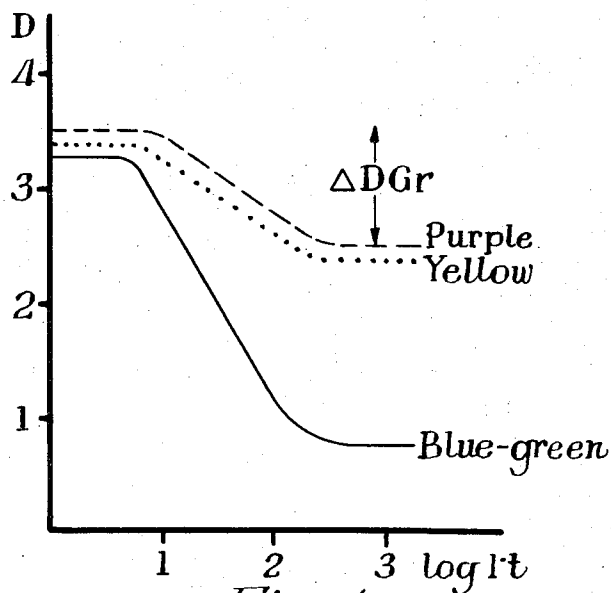


Fig. 1.

Red separation of a highly sensitive color reversal film

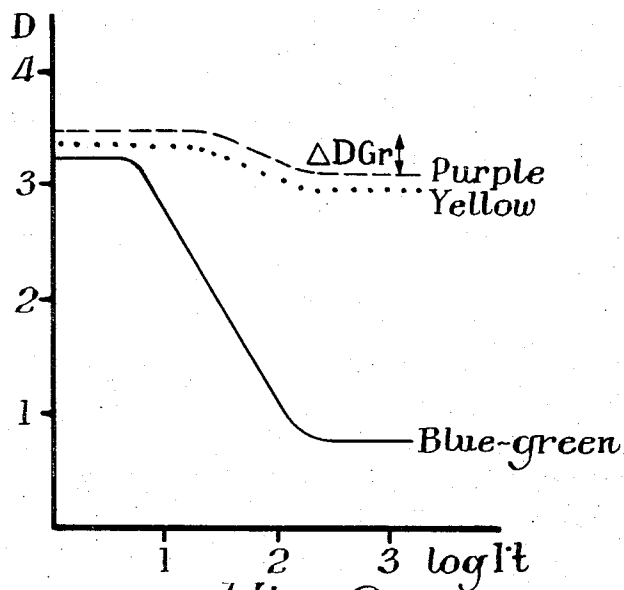


Fig. 2.

Red separation of a moderately sensitive color reversal film

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3 Sheets-Sheet 2

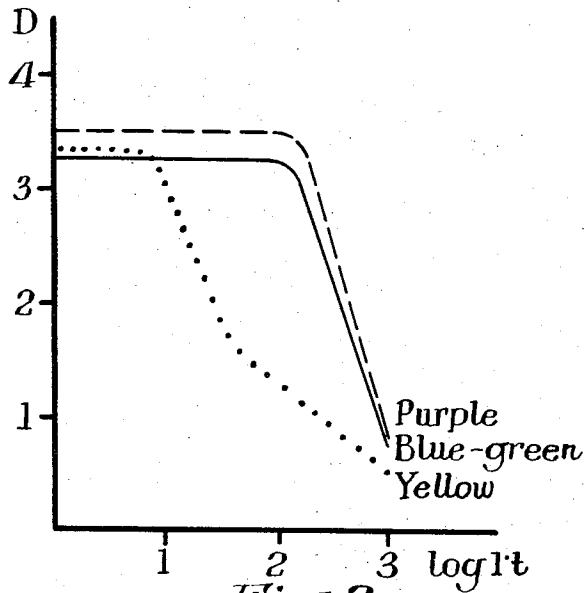


Fig. 3.

Blue separation of a highly sensitive color reversal film

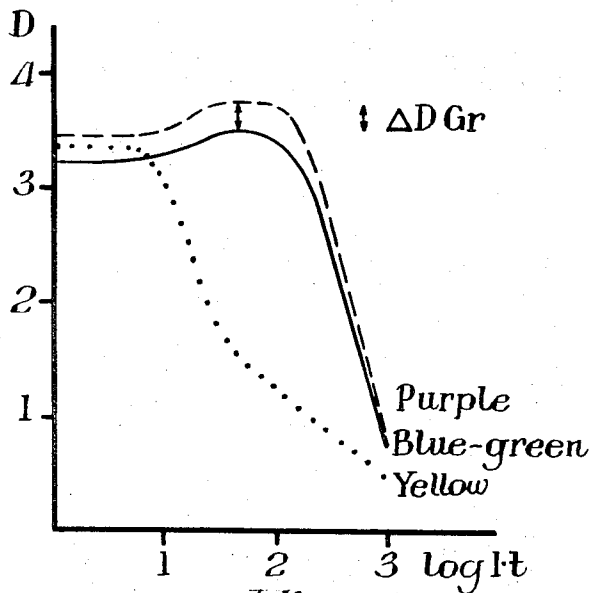


Fig. 4.

Blue separation of a moderately sensitive color reversal film

Fig. 5.

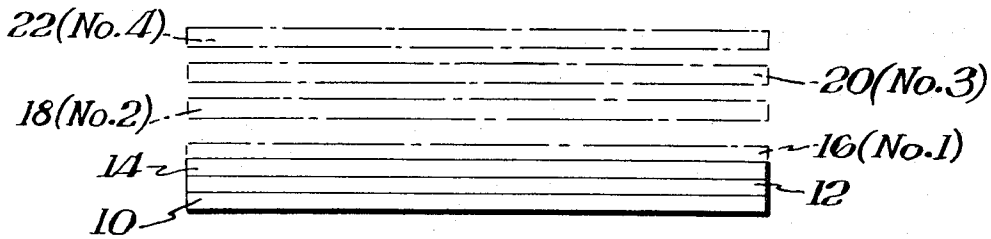


Fig. 6.

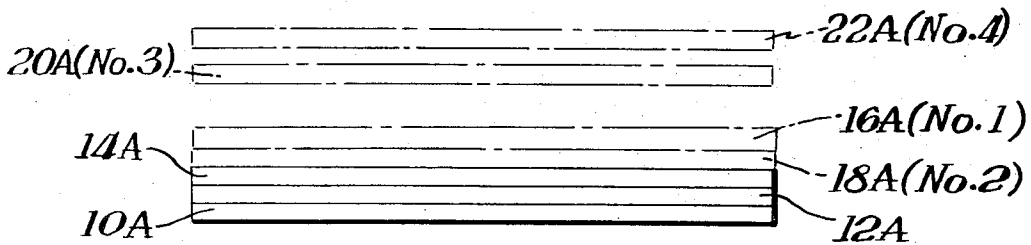
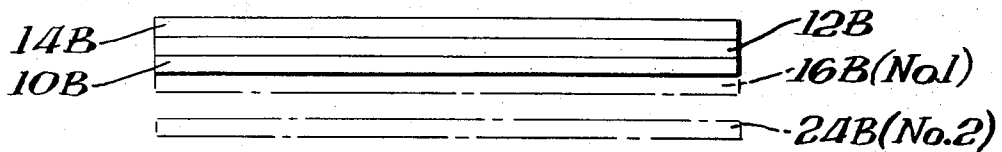


Fig. 7.



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MULTILAYER COLOR PHOTOGRAPHIC MATERIAL

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14 Claims

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SUMMARY

It has now been found that the color reproduction of color reversal materials may be improved if over the uppermost or under the lowermost light-sensitive emulsion layer or between the layers, at least one spectral sensitized, fine-grained silver halide emulsion is arranged with a grain diameter under 1μ . These correcting emulsions are normally sensitized for the red, green or blue-green spectral region, but may also be employed in the unsensitized state in correcting layers, which lie over the uppermost or under the lowermost color-coupler containing emulsion layer. The correcting layers are not coordinated to the picture-synthesizing coupler-containing layers with regard to the sensitivity and also do not contribute to the picture synthesis. Their improving effect on the color reproduction presumably rests on a differentiated influence of the fog and exposure nuclei in adjacent layers during first development (black and white development) and eventually also in the color development of the reversal process.

As the sensitizers for the correcting layers, cyanine dyes, customarily used in color emulsions, may be employed for the red, green, and blue-green spectral range. The amount of sensitizer is so chosen that the improvement of the color reproduction is optimum and empirically is between 30 and 300 mg. dye per mol silver halide.

Fine-grained silverbromiodine emulsions, preferably silverchloride, and silverbromochloride emulsions with a diameter of the silver halide grains of less than 1μ are suitable as the emulsions for the correcting layer. The extent of the influence on the color reproduction is dependent on the composition and the fine-granulation of the correcting layer and on the silver content of the correcting layer. The optimum coating with silver chloride and silverbromochloride emulsions is under 0.8 g. silver halide per square meter. The invention is subsequently explained in more detail by means of examples.

BRIEF DESCRIPTION OF THE DRAWING

Novel features and advantages of the present invention will become apparent to one skilled in the art from a reading of the following description in conjunction with the accompanying drawings wherein similar reference characters refer to similar parts and in which:

FIG. 1 is a densogram of a red filter separation for a highly sensitive color reversal film;

FIG. 2 is a densogram similar to FIG. 1 for a moderately sensitive color reversal film;

FIG. 3 is a densogram of a blue filter separation for a highly sensitive color reversal film;

FIG. 4 is a densogram similar to FIG. 3 for a moderately sensitive color reversal film;

FIG. 5 is a schematic view in elevation of a multilayer photographic material which illustrates one embodiment of this invention;

FIG. 6 is a schematic view in elevation of a multilayer photographic material which illustrates another embodiment of this invention; and

FIG. 7 is a schematic view in elevation of a multilayer photographic material which illustrates a further embodiment of this invention.

Example 1

A high sensitive color reversal film with ca. 23 DIN and normal layer sequence is first synthesized without protective layer as shown in FIG. 5. Mixtures of a high sensitive, coarsely grained silverbromiodide emulsion and a moderately sensitive, finely grained silverbromiodide emulsion, which is ripened with gold, are employed as the emulsions for the cyan layer 10 and magenta layer 12. The yellow layer 14 arranged at the top contains only the coarsely grained emulsion. Aside from the customary

ABSTRACT OF THE DISCLOSURE

To improve the color reproduction of a multi-layer color reversal material, at least one correcting layer of a fine-grained silver halide emulsion having a grain diameter below 1μ is incorporated in the material. It may be disposed over the uppermost, under the lowermost or between the active emulsion layers. The correcting layer may be spectrally sensitized or unsensitized, may be ripened with gold and may include a single halide or a mixture of several.

BACKGROUND OF THE INVENTION

The invention relates to a multi-layer material for color reversal processes, whose color reproduction is improved by incorporation of fine-grained silver halide emulsions.

It is an empirical fact that in color reversal materials, the purity of the reproduced color, the so-called color brilliancy, depends not only on color couplers, sensitizers, filter dyes, and on the type of developing used but also on that the composition and the class of sensitivity of the photographic emulsions used in individual layers exert a certain influence on the color reproduction. This emulsion influence in combination with the developing process is a kind of interimage effect, which describes the sensitometric interactions, which act advantageously or disadvantageously, between the individual layers of a multilayer material.

In the synthesis of the color reversal materials, it is observed that good color brilliancy is the more difficult to achieve, the more sensitive and hence the more coarse-grained the employed emulsions are. This is true above all for the uppermost blue-sensitive and yellow-coupler-containing emulsion layer. Coarse-grained emulsions—those with silver halide grains up to 2 and 3μ diameter—in the yellow layer effect a poorer color reproduction—independent of the type of emulsion and the graininess in the layers underneath—particularly in the red and blue, than fine-grained emulsions. The quality of the color reproduction of a multi-layer reversal material in the red and blue may be determined, besides by means of practical exposures, also by exposing a sensitometer wedge with red or blue light and measuring the wedges, developed in a color reversal developer, on a densitometer behind red, green and blue filters. In FIGS. 1 to 4 are illustrated such densograms of filter separations for a highly sensitive color reversal film of ca. 23 DIN and a moderately sensitive one of ca. 18 DIN. The good color brilliancy of the moderately sensitive film is expressed in Diagrams 2 and 4 by nearly horizontally proceeding curves behind green and blue filters with red separation and by a curve rise with a peak behind green and red filters with blue separation. The poorer color brilliancy of the high sensitive film (FIGS. 1 and 3) is characterized by a strong decline of the corresponding curves with red separation and by the disappearance of the curve rise with respect to blue separation.

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stabilizers, wetting agents, hardening agents, and plasticizers, the individual layers containing the following color couplers and sensitizers:

Cyan layer: α -oxynaphthoyl-N-octadecylamide, 5,5'-dichloro-3,3'-di(β -carboxyethyl) - 9-ethylthiacarbocyanine iodide

Magenta layer: 1-(2',4',6'-trichlorophenyl)-3-(4''-chloro-6''-tetradecylphenoxy-carbonamido) - pyrazolone - (5), 5-(3-ethyl-2,3-benzothiazolydene) - 3-carboxymethyl (rhodanine)

Yellow filter layer: 1-(2',4',6'-trichlorophenyl)-3-undecyl-4(2''-carboxymethoxycinnamal)-pyrazolone-(5)

Yellow layer: 2-tetradecyloxy- α -benzoyl-acetanilide

Four different correcting layers were coated on the top yellow layer of the high sensitive multilayer material. The first layer 16 consisted only of a customary gelatin protective layer. The three others 18, 20 and 22 contained, in different dilution with gelatin, a fine-grained, gold-ripened silverbromiodide emulsion with 4.1 mol percent AgI and ca. 0.5 μ maximum grain diameter. To this emulsion were added 250 mg. of the red sensitizer, such as described for the cyan layer, per mol silver halide.

After exposure of a sensitometer wedge behind a red filter or blue filter on the four materials, they were developed in accordance with the following formula:

- (1) 12 minutes at 24° C. in a thiocyanate-containing Metol hydroquinone first developer
- (2) Washing
- (3) Second exposure
- (4) 15 minutes at 24° C. in a color developer which contains the developing substance diethylamino-o-toluidine hydrochloride and subsequently washed, bleached and fixed in a known manner.

The developed color separation wedges were measured with an Ansco densitometer behind red, green and blue filters. From the densograms, which are similar to those in FIGS. 1 to 4, the decline in the red separation or the rise in the blue separation of the green filter curve ΔDGr was taken and from that the percentage of the change of the green filter density

$$\frac{\Delta DGr}{DGr}$$

was calculated, DGr being the green filter density in the relative exposure=0.

In Table 1 these percentages of change of the green filter density with respect to the red and blue separation are given together with the four different correcting layers:

TABLE 1

No.	Correcting layer	$\Delta DGr/DGr$ Red separation, percent	$\Delta DGr/DGr$ Blue separation, percent
1.....	Gelatin layer.....	-31	+3
2.....	Fine-grained AgBr/AgI-emulsion 1:3 diluted.	-23	+5
3.....	Fine-grained AgBr/AgI-emulsion 1:1 diluted.	-18	+7
4.....	Fine-grained AgBr/AgI-emulsion undiluted.	-13	+9

It is seen how with increasing content in the correcting layers of fine-grained, red-sensitized emulsion

$$\frac{\Delta DGr}{DGr}$$

becomes less and less negative with red separation and more and more positive with blue separation. Thus is obtained a color brilliancy which corresponds to a moderately sensitive multi-layer material.

Example 2

The color reversal material differs from Example 1 in that in the cyan layer 10 and magenta layer 12 there was used only a moderately sensitive silverbromiodide emulsion instead of a mixture of highly and moderately sensitive emulsion; but in the yellow layer there was used

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the same coarse-grained emulsion as in Example 1. The combined sensitivity of the material according to Example 2 was lower by 3 DIN than that of Example 1. Besides this, the arrangement of layers and the correcting layers on top of the yellow layer correspond to those of Example 1. The test results are illustrated in the following table.

TABLE 2

No.	Correcting layer	$\Delta DGr/DGr$ Red separation, percent	$\Delta DGr/DGr$ Blue separation, percent
1.....	Gelatin layer.....	-27	0
2.....	Fine-grained AgBr/AgI-emulsion 1:3 diluted.	-20	+5
3.....	Fine-grained AgBr/AgI-emulsion 1:1 diluted.	-10	+6
4.....	Fine-grained AgBr/AgI-emulsion undiluted.	-13	+8

Example 2 shows that the improvement of the color brilliancy sets in independent of whether in both of the lower emulsion layers there are contained coarsely grained, highly sensitive emulsions in a mixture with moderately sensitive emulsions or the latter alone.

Example 3

The material differs from that of Example 2 in that the correcting layers 18A, 20A and 22A are inserted between the yellow filter layer 16A and yellow layer 14A. Only the red separation was measured.

TABLE 3

No.	Correcting layer	$\Delta DGr/DGr$ Red separation, percent
1.....	Gelatin layer.....	-27
2.....	Fine-grained AgBr/AgI-emulsion 1:3 diluted.....	-20
3.....	Fine-grained AgBr/AgI-emulsion 1:1 diluted.....	-18
4.....	Fine-grained AgBr/AgI-emulsion undiluted.....	-16

Example 3 shows that the correcting layers, arranged under the yellow layer, also improve the color brilliancy but in a lesser measure than in the arrangement over the yellow layer.

Example 4

The material differs from that in Example 1 in that for the correcting layers 18, 20 and 22 there is employed a fine-grained silver bromochloride emulsion with 75 mol percent AgCl and 25 mol percent AgBr, sensitized with the red sensitizer of Example 1.

TABLE 4

No.	Correcting layer	AgX- content, g./m. ²	$\Delta DGr/DGr$ Red separation, percent
1.....	Gelatin layer.....	0	-31
2.....	AgCl/AgBr-emulsion.....	0.3	-20
3.....	do.....	0.5	-17

With a sensitized silverbromochloride emulsion in the correcting layer, it is possible to achieve a clear improvement of the color brilliancy even with a moderate silver content.

Example 5

A color reversal film contained, as in Example 2, for the cyan layer 10 and magenta layer 12, a semi-sensitive silver bromiodide emulsion; in the uppermost arranged yellow layer 14, a coarsely grained emulsion. Onto the yellow layer 14 layers of varying composition were coated. The first layer 16 consisting of a customary gelatin protective layer, layer 18 of a gelatin diluted, fine-grained, gold-ripened, unsensitized silverbromiodide emulsion according to Example 1, and layer 20 of the same emulsion but sensitized for the red spectral range with 5,5'-dichloro-

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3,3'-di-(β -carboxyethyl) - 9 - ethylbenzothiocarbocyanine iodide. There is no layer 22 in this example.

TABLE 5

No.	Correcting layer	$\Delta DGr/DGr$ Red separation, percent
1-----	Gelatin layer-----	-27
2-----	Unsensitized AgBr/AgI-emulsion-----	-20
3-----	Red-sensitized AgBr/AgI-emulsion-----	-15

It is seen that even an unsensitized, fine-grained emulsion clearly improved the color brilliancy. By spectral sensitization of the emulsion, the effect may still be increased.

Example 6

As shown in FIG. 7, under the cyan layer 10B of a high sensitive color reversal film, such as in Example 1, there was coated a correcting layer 24B which consisted of a diluted, fine-grained silverbromochloride emulsion, as in Example 4, sensitized with 5-(3-ethyl-2,3-benzothiazolylidene)-3-carboxymethylrhodamine for the cyan spectral range and which contained 0.6 g. AgClBr/m.². This material was compared with a corresponding one without correcting layer with respect to color brilliancy of the red separation.

TABLE 6

No.	Correcting layer	$\Delta DGr/DGr$ Red separation, percent
1-----	Without-----	-33
2-----	Under the cyan layer-----	-19

The effect of the correcting layer under the cyan layer is clearly apparent.

We claim:

1. A multilayer photographic material incorporating color components for color reversal processes, and having a number of combined coupler-containing and dye-producing silver halide emulsion layers in a layer arrangement, said arrangement being characterized by the disposition of at least one additional layer, comprising a spectrally sensitized, fine-grained silver halide emulsion with a grain diameter below 1μ in direct proximity to one of said combined coupler-containing and dye-producing silver halide emulsion layers taking part in the layer arrangement whereby the color reproduction of said material is improved, the spectral sensitivity of said additional layer being uncoordinated with the sensitivity of the combined coupler-containing and dye-producing silver halide emulsion layers and therefore said additional layer does not contribute to the picture image production but advantageously influences fog and exposure nuclei in adjacent dye producing layers to thereby improve the color reproduction of said material.

2. A multilayer photographic material incorporating color components for color reversal processes, and having an uppermost and undermost layer each containing color coupler and silver halide emulsion, said material being characterized by the arrangement of an additional layer consisting of an unsensitized, fine-grained silver halide emulsion with a grain diameter below 1μ over said uppermost or under said lowermost emulsion layer containing color coupler and silver halide emulsion whereby the color reproduction of said material is improved, the spec-

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tral sensitivity of said additional layer being uncoordinated with the sensitivity of the uppermost of lowermost color coupler and silver halide emulsion layers and therefore said additional layer does not contribute to the picture image production but advantageously influences the fog and exposure nuclei in adjacent color coupler and silver halide emulsion-containing layers to thereby improve the color reproduction of said material.

3. A multilayer photographic material as set forth in claim 1, characterized in that said additional layer is a member of the group consisting of silver chloride emulsions, silverbromochloride and silver bromiodine emulsions and having a grain diameter below 1μ .

4. A multilayer photographic material as set forth in claim 1 wherein said silver halide emulsion comprises a single halide or a mixture of several.

5. A multilayer photographic material as set forth in claim 1 wherein said silver halide emulsion is gold-ripened.

6. A multilayer photographic material as set forth in claim 1 wherein a number of additional layers are provided.

7. A multilayer photographic material as set forth in claim 1 wherein said multilayer material includes filter layers and dye-producing layers and said additional layer is inserted between one of said filter layers and one of said dye-producing layers.

8. A multilayer photographic material as set forth in claim 1 wherein said material includes dye-providing layers and filter layers and said additional layer is inserted under one of said dye-producing layers.

9. A multilayer photographic material as set forth in claim 1 also including an unsensitized additional layer.

10. A multilayer photographic material as set forth in claim 1 wherein a number of said additional layers are provided and said layers are spectrally sensitized for different colors.

11. A multilayer photographic material as set forth in claim 1 wherein said additional layer includes a sensitizer and said sensitizer being present in the approximate amount of 30 to 300 mg. dye per mol of emulsion.

12. A multilayer photographic material as set forth in claim 11 wherein said sensitizer is a cyanine dye.

13. A multilayer photographic material as set forth in claim 4 wherein said additional layer has less than 0.8 g. silver halide per square meter.

14. A multilayer photographic material as set forth in claim 2 wherein said additional layer is transparent.

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