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 PHOTOGRAPHIC SILVER HALIDE MULTILAYER MATERIAL
 FOR CORRECTING INADEQUATE CONTRAST
 Filed April 6, 1964

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FIG. 1



FIG. 2

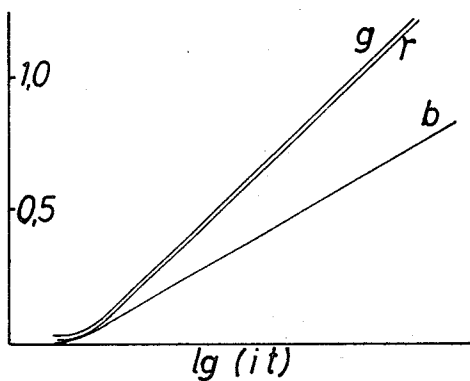


FIG. 3

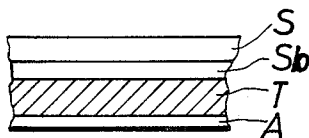
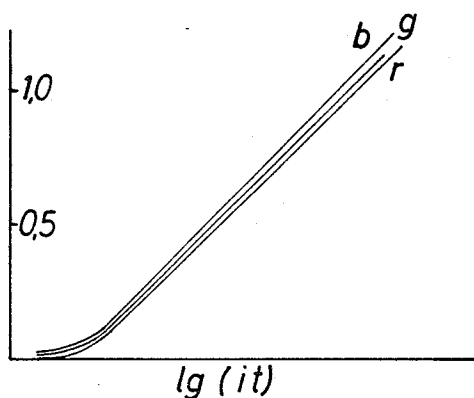


FIG. 4



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PHOTOGRAPHIC SILVER HALIDE MULTILAYER MATERIAL FOR CORRECTING INADEQUATE CONTRAST

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ABSTRACT OF THE DISCLOSURE

Single film used for separate high quality continuous tone color separation records for all colors, gives more uniform contrast for the different colors and these records are more uniformly processed by bringing up the contrast of one or more colors, generally blue, inherently having less contrast. This is effected by combining the usual emulsion with a superposed emulsion of the same speed, sensitive only to the low contrast color or colors, and having a thickness that contributes the desired contrast build-up.

This invention relates to a multilayer light-sensitive photographic material which under the same conditions of development provides images of equal gradation, independently of the type of light used on exposure.

It is known that the gamma response of a light-sensitive silver halide emulsion layer depends on the color of the light to which the layer is exposed. Thus, the gradation of spectrally sensitized silver halide emulsion layers is steeper in the region of spectral sensitization than in the region of the natural blue sensitivity of the silver halide. This property of all silver halide emulsions results from the fact that small silver halide grains are more strongly sensitized by dyestuffs than larger grains. Considerable disadvantages are found to be associated with this property in practice, especially in the production of color separation records. Thus, when reproducing multi-color originals, the gradation of the blue filter separation record produced with blue light is always considerably softer than the gradation of the green filter or red filter separation. Since all three color separation records must have the same gradation for technical reproduction reasons, it is necessary to develop them in different ways, either the green and red filter separation records being processed for a shorter time or the blue filter separation record for a longer time. This fact is extremely inconvenient in practice and it is particularly disadvantageous in connection with automatic processing which is being increasingly introduced, since in this type of processing it is only possible for all color separation records to be treated in similar manner.

The magnitude of the differences in the gradations of the three color separation records with normal commercial panchromatic films is illustrated by a typical material in which the gamma of the blue filter separation record after a development time of 4 minutes is 0.8, whereas the green filter separation record reaches the same gamma in a development time of 1 minute and the red filter separation record reaches this value in an even shorter time. Any person skilled in the art knows that a satisfactory color set cannot be produced under such varying development conditions. If it is desired to produce a gamma of 1.2 with this material the red filter record must be developed for 2½ minutes and the green for 4 minutes. With blue light, the required gamma of 1.2 cannot be produced at all, since gamma only amounts to

0.85 even with longest possible development (infinite). Even with a very hard operating p-aminophenol-hydroquinone developer (a so-called line developer), a gamma value of only 1.0 is obtained. Therefore, in practice, the only possibility is to use from the start a film material with a higher gamma for the blue filter separation record. However, experience shows that this produces disadvantages as far as the adaptation of the color separation records and their optical uniformity (different silver color or initial coloring of the gelatine) are concerned, apart from other difficulties which arise in keeping on hand two types of film.

It has now been found that these disadvantages can be overcome by the use of a special photographic material. This material comprises at least two silver halide emulsion layers coated on a common support, one of said layers being spectrally sensitized and having a lower gamma response to light out of first regions of the spectrum as compared with the gamma response to light out of second regions of the spectrum, the other of said layers being sensitive only to light out of said first regions of the spectrum having the same speed as the spectrally sensitized layer when exposed to this light and having a gamma response which is essentially equal to the difference between the gamma response of said spectrally sensitized layer to light out of said first and said second regions of the spectrum, said material having essentially the same gamma response to light out of different regions of the spectrum for which said spectrally sensitized layer is sensitive.

A material which contains a panchromatic light-sensitive silver halide emulsion layer and an additional silver halide emulsion layer which is sensitive to blue light only, is of particular importance for correcting the relatively low gamma response of the panchromatic layer to exposure by blue light. This material is therefore a two-layer film, comprising as sole light-sensitive layers a panchromatic silver halide emulsion layer, i.e., a layer spectrally sensitized for the green and red third of the spectrum and by its nature sensitive to light of the blue third of the spectrum, and a second silver halide emulsion layer which is only blue-sensitive. The layer thickness of the second layer depends on how strongly the gamma response of the upper layer differs with respect to its gamma response to blue light and its gamma response to green and red light. It is obvious that a small difference in gamma is to be corrected by a comparatively thin blue-sensitive layer, whereas a comparatively thick blue-sensitive layer is necessary for correcting a large difference in gammas. The layer thickness best suited to the actual case can be easily established by a few experiments.

The two light-sensitive layers can be arranged either on the same side or on opposite sides of the support. In the latter case, the support must of course be transparent. In all cases, the arrangement of the layers which is to be preferred is that in which the layer to be corrected faces the light source and therefore the correcting layer faces away from the light source. However, it is also possible to use the opposite layer sequence. With the aforementioned panchromatic color separation record film, the panchromatically sensitized layer is advantageously the uppermost layer when the layers are arranged on one side, the blue-sensitive layer (correcting layer) being arranged therebeneath as the layer adjacent the support.

The photographic material according to the invention is particularly suitable for the production of color separation records. In contrast to the known normal commercial materials for this purpose, color separation records (generally three namely the green, red and blue filter records) are, pursuant to the present invention, obtained with practically identical gradation. In this way, it be-

comes possible for the processing operator to produce satisfactory color sets by the simplest possible means and in the last possible time.

The invention is illustrated by the accompanying drawings.

FIGURE 1 represents a cross-section of a normal commercial panchromatic silver halide film. In this figure, T is a transparent support, S is a panchromatic silver halide emulsion layer and A is an antihalation layer. The density curves for this material after exposure to blue light (b), green light (g) and red light (r) and development under the same conditions are shown in FIGURE 2. The lower gamma response to blue light is clearly apparent, this being $\gamma_b=0.60$, as compared with the other two gammas $\gamma_g=\gamma_r=1.0$. FIGURE 3 represents a preferred form of the material according to the invention. In this, the material of FIGURE 1 now is combined with a second silver halide emulsion layer S_b , which in this case is arranged between the panchromatic layer S and the support T and which is only blue-sensitive.

The gradations of the two-layer material on exposure to blue, green and red light are shown in FIGURE 4. There is no change from FIGURE 2 as regards the gamma response to green and red light, since the layer S_b is not sensitive to green and red light, is therefore not affected, and consequently contributes nothing to their density. However, when exposed to blue light, the layer S_b is also exposed, which leads to an increase of the gamma response to this light, so that now all three gammas have essentially the same values.

The photographic material according to the invention can be produced in the usual manner, for example, in accordance with the following general data:

An emulsion prepared by one of the conventional methods (see Glafkides, "Photographic Chemistry," vol. I, Fountain Press, London, 1958), is applied to the usual transparent film supports of glass, cellulose esters, polystyrene, polycarbonates or polyesters of terephthalic acid and glycols. The emulsion may be ripened up to maximum sensitivity after addition of chemical sensitizers, such as sulphur compounds of the thiosulphate or thiosinamine type, and noble metals such as gold, palladium, ruthenium, Onium salts, for example, ammonium, sulphonium and phosphonium salts, as well as polyethylene oxides, can also be added for increasing the sensitivity.

Prior to casting, the emulsion also has added thereto in the usual way wetting agents, for example saponin, stabilizers against storage fogging, such as 5-methyl-7-hydroxy-1,3,4-triazolindolizine, as well as spectral sensitizers, e.g., cyanines or merocyanines.

According to conventional ideas concerning the absorption and dispersion power of light-sensitive layers, the sensitivity of a layer is lowered if a second light-sensitive layer is arranged above it, since this second layer obviously absorbs light. Consequently, it would be necessary to select for the layer facing away from the light source an emulsion which would have a higher sensitivity to the light to which both layers are sensitive; in the combination of the present invention this layer facing away from the light is the one which is only blue-sensitive. However, since panchromatic color separation record films must have the highest sensitivity which can be achieved, it is not possible under the given conditions (e.g., of graininess and gradation) to find a layer which is more highly sensitive than the layer facing the light source. Accordingly, a lowering of the sensitivity would be associated with the use of the process according to the invention, whereby the value of such a process would be quite considerably reduced.

It was surprisingly found that the light sensitivity of the material according to the invention, more especially the sensitivity of the layer facing away from the light source, is maintained if both layers, each measured separately, have the same sensitivity in the common spectral sensitivity region. This condition is, in particular, satis-

fied if the same emulsion is used for both layers, only one being spectrally sensitized and the other not. Thus the highest sensitivity which is reached with the panchromatic layer is still maintained.

The present invention is not limited to the examples described. Instead of a panchromatic emulsion, whose gamma response to blue light is too low and has in consequence to be increased by a correcting layer, it is also possible to use an orthochromatic layer having an insufficient gamma response to blue light. On the other hand, it may be necessary in certain cases to increase the steepness of the gradation for a type of light other than blue light, e.g., for green light. In such a case the correcting layer must only be green-sensitive and the natural blue sensitivity of the correcting layer must be suppressed by known means, such as by a dyeing with yellow dyestuff which is removed by the processing baths (e.g. tartrazin), or by use of a correspondingly colored intermediate gelatin layer. Furthermore, it is also possible for the differing gamma response to three types of light, e.g., to blue, green and red light, to be eliminated according to the invention by first of all raising the middle of the three gammas by a correcting layer to the value of the highest gamma and, in analogous manner, bringing up the lowest gamma by another correcting layer according to the invention to the level of the other two gammas. For example, if the gamma responses of a panchromatic reproduction film to blue, green and red light are 0.8, 1.1 and 1.3, then by means of an orthochromatic correcting layer of certain thickness, the gamma response to green light is raised by 0.2 and simultaneously to blue light by 0.15. The two-layer color film therefore has the gammas 0.95, 1.3 and 1.3. Now, by means of a second correcting layer which is only blue-sensitive, the total gamma response to blue light is raised from 0.95 to 1.3, so that the film now has the same gammas of 1.3 in all three regions of the spectrum.

The process is not restricted to the visible spectrum. The said spectral regions can also lie in other regions to whose radiation the film is sensitive, more especially in the ultraviolet or in the infrared regions.

Example

A gelatine-silver bromiodide emulsion (the silver salt of which contains 2.5 mol percent of silver iodide, the silver-gelatine ratio of which is 1:0.85, the speed and gamma being those of an emulsion ordinarily used for the preparation of color separation record films) is divided into two portions (A and B).

Portion A is cast without spectral sensitizers on to a polycarbonate support which is 0.2 mm. thick and which carries a subbing layer. On the other side, the support is provided with a dark green antihalation layer with a thickness of 10 microns. The layer thickness of the light-sensitive layer after drying is 4 microns and it has 2.5 g. of Ag/m². The gamma of this layer, when developed for 3 minutes in the developer indicated below and additionally diluted with 1 part of water, amounts to $\gamma=0.40$. The portion B of the emulsion is cast on to this first layer, and the said portion B, in contrast to portion A, also has added spectral sensitizers for the green and red third of the spectrum. The layer thickness of the second layer after drying is 8 microns and it has 4.95 g. of Ag/m². The total thickness of the two layers is therefore 12 microns and the total silver coating is 7.4 g. of Ag/m².

Developer:		G.
p-Methylaminophenol sulfate	-----	7.5
Anhydrous sodium sulfite	-----	40
Hydroquinone	-----	3.5
Anhydrous sodium carbonate	-----	30
Potassium bromide	-----	3
Water made up to 1 liter.		

The gradation of the two-layer film, developed for 5 minutes in the said developer, after exposure with strictly blue light (Agfa Reprofilter No. 352), with strictly green

light (Agfa Reprofilter No. 54L) and with strictly red light (Agfa Reprofilter No. 45L) is—

Material according to the invention:

γ_{blue} -----	1.12
γ_{green} -----	1.02
γ_{red} -----	1.05

Same material but without the unsensitized layer:

γ_{blue} -----	0.73
γ_{green} -----	1.00
γ_{red} -----	1.03

What we claim is:

1. In a light-sensitive photographic material for separately making blue, green and red high quality continuous tone color separation records, the improvement according to which the photographic material has a plurality of light-sensitive low contrast superposed silver halide emulsion layers having the same speed, one of the layers being panchromatically sensitized but developing to inadequate contrast when making color separation records for at least one of the three colors as compared to the contrast for a different one of the colors, and the remainder of the emulsion layers being sensitive essentially only to the colors that produce inadequate contrast in the panchromatic layer, and being of a thickness that provides a contrast equal to the difference between (a) the contrast produced by the panchromatic layer alone for the color separation records of inadequate contrast and (b) the contrast produced by the panchromatic layer alone for the color separation of adequate contrast, said thickness being directly related to said difference.

2. The combination of claim 1 in which aside from spectral sensitizing the layers all have the same emulsion.

3. The combination of claim 1 in which the adequate contrast is approximately 1.

4. The combination of claim 2 in which the emulsion is an iodobromide emulsion.

5. The combination of claim 1 in which the layers are coated over each other and the panchromatic layer is the outermost layer.

6. In a light-sensitive photographic material for directly making separate high quality continuous tone color separation records for all colors, the improvement according to which the photographic material has two light-sensitive low contrast superposed silver halide emulsion layers having the same speed, one of the layers being panchromatically sensitized but developing to inadequate contrast when making a blue color separation record as compared to the contrasts developed for other color separation records, and the second emulsion layer being sensitive essentially only to blue and being of a thickness that provides a contrast equal to the difference between (a) the contrast provided by the panchromatic emulsion alone for the blue separation record and (b) the contrasts provided by the panchromatic emulsion alone for the other separation records, said thickness being directly related to said difference.

7. The combination of claim 6 in which the emulsion of the second layer is spectrally unsensitized but otherwise the same emulsion as that in the panchromatic layer.

8. The combination of claim 6 in which the contrasts provided by the panchromatic emulsion alone for the colors other than blue, are approximately 1.

9. The combination of claim 7 in which the emulsion is an iodobromide emulsion.

10. The combination of claim 6 in which the layers are coated over each other and the panchromatic layer is the outermost layer.

11. The combination of claim 1 in which the panchromatic layer alone provides inadequate contrast for blue and green color separation records and the emulsion layers include an orthochromatic emulsion that brings up the contrast of both the blue and the green color separation records.

References Cited

UNITED STATES PATENTS

1,910,877	5/1933	Baker	96—70
1,994,627	3/1935	Von Biehler	96—70

J. TRAVIS BROWN, *Primary Examiner*.