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MULTILAYER PHOTOGRAPHIC FILM HAVING IMPROVED RESOLVING POWER

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FIG. 1.

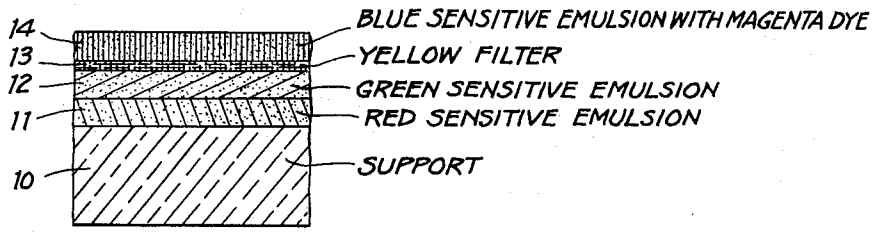


FIG. 2.

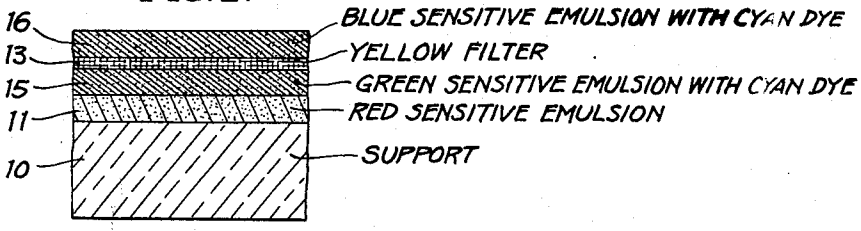


FIG. 3.

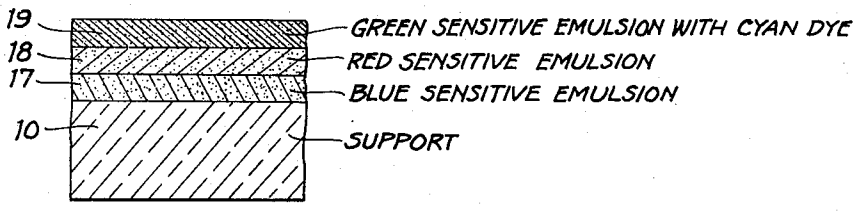
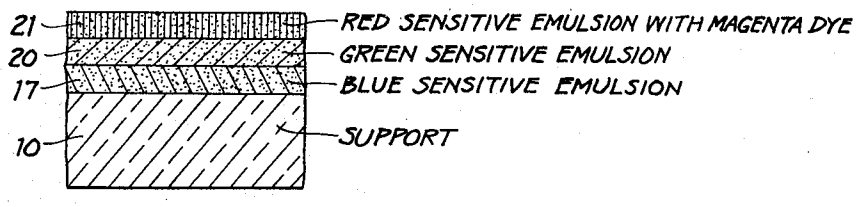


FIG. 4.



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MULTILAYER PHOTOGRAPHIC FILM HAVING IMPROVED RESOLVING POWER

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1 Claim. (Cl. 95—2)

This invention relates to photography and particularly to a multi-layer photographic color film having improved resolving power.

In the usual sensitivity arrangement of three-layer photographic film, the red-sensitive emulsion layer is coated adjacent the support and this is followed in order by the green-sensitive emulsion layer and the blue-sensitive emulsion layer. It is customary to form a cyan dye image in the red-sensitive layer, a magenta dye image in the green-sensitive layer and a yellow dye image in the blue-sensitive layer. It is also known that a different sensitivity arrangement may be used in which either the red sensitive layer or the green-sensitive layer is coated outermost for the purpose of improving definition.

In any of these types of the multi-layer film, the light forming the image in the lower layers must first pass through an upper layer or layers. For example, in film having the usual sensitivity arrangement, red, green, blue from the support outward, the light forming the image in the red-sensitive layer must first pass through the blue-sensitive top layer, the green-sensitive middle layer and any other layers which intervene. Since these top layers are optically turbid, they tend to impair the definition and therefore the quality of the image formed in the lower layer or layers. This is due to the light-scattering effect of the turbid upper layers and this, in turn, reduces the quality of the entire picture.

It is therefore an object of the present invention to provide a method for improving the resolving power of the lower layers of a multi-layer color film. A further object is to provide a novel multi-layer photographic film.

These objects are accomplished by incorporating in an upper layer of a multi-layer film, a coloring material which absorbs a part but not all of the light which the lower layer or layers record.

The accompanying drawing shows in sectional views films constructed according to our invention.

The film used according to our invention consists of a suitable support such as cellulose ester, synthetic resin or paper, having on one side thereof suitable subbing layers and three superposed silver halide emulsion layers. In the usual sensitivity arrangement, the red-sensitive silver halide emulsion layer is coated on the subbing layer and that is followed by the green-sensitive emulsion layer and the blue-sensitive emulsion layer. A removable yellow coloring material is ordinarily contained in a layer between the blue-sensitive emulsion layer and the green-sensitive emulsion layer, and other intermediate or overcoating layers may also be present. This sensitivity arrangement may be altered by coating the red-sensitive emulsion layer or the green-sensitive emulsion layer outermost, especially where the film is designed as a print material.

The silver halide emulsion layers may contain couplers incorporated in any suitable way, for example, in the manner described in Jelley and Vittum U. S. Patent 2,322,027. When such couplers are used, the cyan-forming coupler will ordinarily be incorporated in the red-sensitive emulsion layer, the magenta-forming coupler in the green-sensitive emulsion layer and the yellow-forming coupler in the blue-sensitive emulsion layer. If the film is to be used as a negative taking material colored couplers for masking purposes may be employed as described in Hanson U. S. Patent 2,449,966.

According to our invention, resolving power or definition or both are improved by incorporating in an upper

emulsion layer of the film a material which may be a dye or pigment and which absorbs part of the light which a lower silver halide layer records but transmits light which the silver halide layers above the lower layer record. For example, in a multi-layer film having the sensitivity arrangement red, green, blue, from the support outerward, the blue-sensitive top layer may contain a magenta or reddish dye which absorbs part of the light which the green-sensitive layer records. Either the blue-sensitive layer or the green-sensitive layer may contain a cyan or bluish dye which absorbs part of the light which the red-sensitive layer records. These dyes do not absorb light to which the layer in which they are incorporated is sensitive or the light to which any layer above the layer in which they are incorporated is sensitive.

The dye or pigment incorporated in the emulsion layer inevitably produces a loss in speed of the layer below that in which it is incorporated. For this reason, the density of the absorber incorporated in any layer should be held to the minimum required to give the necessary improvement in image sharpness. In a camera film, an optical density of 0.3 would be about the upper limit but in printing or duplicating films, an optical density of about 0.6 may be tolerated. An optical density of 0.6 means that the dye or pigment absorbs ¾ of the light impinging on it in the spectral region of maximum absorption of the absorbing material. Thus the absorbing material which we employ should not absorb more than about ¾ of the light which impinges on it in the spectral region of maximum absorption of the dye or pigment.

Coloring materials which we may employ are the aluminum lake of aurin tricarboxylic acid and Prussian Blue. The aurin tricarboxylic acid is a magenta dye and is removed during processing by an alkali sulfite solution, for example, a developing solution. Prussian Blue is a bluish pigment which is removed in an alkaline developing solution containing iron sequestering agents such as ethylene diamine tetra-acetic acid.

The following examples illustrate the method of using the coloring materials according to our invention.

Example 1

"Turnbull's Blue" in gelatin was prepared by taking 180 cc. of a solution of gelatin in water, 4.0 g./100 cc. at pH 2.5 to 3.0. To this, at 40° C., there was added simultaneously a solution of 3.6 g. of ferrous ammonium sulfate in 36 cc. of water and a solution of 3.0 g. of potassium ferricyanide in 36 cc. of water. The solutions were run in slowly over a period of three minutes with continuous mechanical stirring. The dispersion was chilled until the gelatin was thoroughly set, then shredded and washed in running water for three hours to remove soluble by-products and excess potassium ferricyanide.

This disperson may be added to emulsion. The color is bleached by the alkali of the developer; materials forming complexes with ferric iron, such as ethylenediamine tetra-acetic acid or sodium fluoride, may be added to the developer to avoid the possibility of stain from the ferric hydroxide which is formed.

Example 2

The dispersion of the aluminum lake of aurin tricarboxylic acid was prepared as follows.

Five-tenths g. of aurin tricarboxylic acid was dissolved in 1 cc. 20% sodium hydroxide and 15 cc. water. To this was added 0.75 g. aluminum sulfate ($18H_2O$) which had first been dissolved in water, precipitated and redissolved by the addition of 20% sodium hydroxide solution.

The above combination was then added to 160 cc. of 2.5% gelatin solution at 40° C. Vigorous stirring was maintained during the addition of the alkaline solution. The pH of the gelatin solution was kept between 5.0–5.5 by the addition of dilute sulfuric acid.

When all the alkaline solution had been added, 40 cc. of 10% gelatin was added. Stirring was continued for 5 minutes. The gelatin solution was chilled, shredded, and washed with cold water for 2 hours.

This may be added to the emulsion with very little desensitization. It is bleached in any developer con-

taining moderate amounts of sulfite or, if the film is processed only in color developer low in sulfite, a separate solution of, for example, 10% sodium sulfite may be used.

The following example describes a complete film structure made according to our invention.

Example 3

Starting with the support, the successive layers for a negative material are as follows:

1. *Red-sensitive layer.*—A bromoiodide emulsion with silver halide corresponding to .86 g. silver per sq. meter. This emulsion is sensitized with 3,3'-dimethyl-9-ethyl-4,5,4',5'-dibenzthiacarbocyanine chloride, about .15 g. per mole of silver halide, the exact amount depending on the grain size of the emulsion. It contains a cyan color former, 2-α(4-amylphenoxybutyrylamino)4-chloro-5-methyl phenol, 650 mg. per sq. meter, dissolved in four times its weight of dibutylphthalate; the solution of the coupler is dispersed in fine droplets in the emulsion.

2. The second coat is an emulsion layer with silver halide corresponding to 1.07 g. silver per sq. meter. This is sensitized to green with 2-diphenylamino-5-[(3-ethylbenzothiazolylidene)-ethylidene]-4-(5)-thiazolone, approximately .15 g. per mole of silver halide, the amount depending on grain size of the emulsion. It contains as a red light absorber Prussian Blue in a colloidal dispersion at a concentration of 0.10 g. per sq. meter. As a magenta color former, there is added 1-(p[p'-tert. butylphenoxy]phenyl) - 3 - (m[p-toluenesulfonylamino]benzoylamino-5-pyrazolone, 550 mg. per sq. meter, dissolved in four times its weight of dibutylphthalate.

3. The third coat is a dispersion of colloidal silver in gelatin, 100 mg. per sq. meter.

4. The fourth coat is an unsensitized bromoiodide emulsion containing silver halide corresponding to .86 g. silver per sq. meter. To this there is added a dispersion of the aluminum lake of aurin tricarboxylic acid in gelatin, .075 g. (calculated as free acid) per sq. meter. It contains a yellow color former, N(p-benzoylacetaminobenzenesulfonyl)-N-(2-phenylpropyl)-p-tert. amylaniline, 1750 mg. per sq. meter, dissolved in four times its weight of dibutylphthalate.

Our invention will now be described by reference to the accompanying drawing. As shown in Fig. 1 thereof, **10** is a support having thereon a red-sensitive silver halide emulsion layer **11**, a green-sensitive silver halide emulsion layer **12**, a yellow filter layer **13** and a blue-sensitive silver halide emulsion layer **14**. The blue-sensitive layer **14** contains a magneta dye which absorbs part of the green light which the layer **12** records and therefore reduces scattering of green light.

Fig. 2 illustrates a similar structure in which the green-sensitive layer **15** and the blue-sensitive layer **16** contain a cyan dye which absorbs part of the light which the red-sensitive layer **11** records and therefore reduces scattering of red light.

In the modification shown in Fig. 3, the blue-sensitive layer **17** is adjacent the support, the red-sensitive layer **18** is next and the green-sensitive layer **19** which contains a cyan dye or pigment is outermost. In this case the cyan dye or pigment in layer **19** reduces scattering of red light which records in layer **18** but does not affect the blue light which records in layer **17**.

Fig. 4 illustrates a modification in which the blue-sensitive layer **17** is adjacent the support, the green-sensitive layer **20** is next and the red-sensitive layer **21** containing a magenta dye or pigment is outermost. In this case the magenta dye or pigment absorbs part of the green light which layer **20** records and thereby reduces scattering of green light.

The films described in Figs. 3 and 4 are intended for printing.

It will be understood that the modifications and examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claim.

We claim:

A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof, silver halide emulsion layers separately sensitive, in order, to the red, green, and blue spectral regions, said red-sensitive emulsion layer being adjacent said support and said green-sensitive emulsion layer containing Prussian Blue as a red-light-absorbing material, said material absorbing not more than ¾ of the red light impinging on it.

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