Fig. 1.

13. Red sensitive AgCl
12. Green sensitive AgCl containing blue dye
11. Blue sensitive AgBr
10.

Fig. 2.

13. Green sensitive AgCl
14. Red sensitive AgCl
15. Blue interlayer
11. Blue sensitive AgBr
10.
This invention relates to photography and particularly to a multi-layer photographic film having a light filtering material incorporated therein.

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 well known that the definition of the resulting color picture is determined to a large extent by the cyan and magenta dyes and that the overall definition can be improved by arranging the three emulsion layers so that the layer containing the cyan or magenta dye is outermost and the layer containing the yellow dye is adjacent the support or farthest from the exposing light.

This arrangement is described, for example, in Baker U. S. Patent 1,867,301 and Tarbin U. S. Patent 1,871,479.

When this inverted sensitivity order is used, it is frequently necessary to employ a blue-sensitive emulsion layer, that is, the layer adjacent the support, having a higher blue light speed than would be required if the blue-sensitive layer were outermost. Whether for this or other reasons, it has been found that the blue-sensitive emulsion layer tends to scatter any red or green light reaching it after passing through the upper layers and thereby to reduce the overall definition of the resulting picture. This is not happening in the bottom layer of the film cancels out the advantages obtained by placing the green-sensitive or red-sensitive layer outermost and is a serious defect in films using this sensitivity arrangement.

It is desired to retain the advantages of coating the green-sensitive or red-sensitive layer outermost in a multi-layer film and at the same time to reduce or overcome the disadvantage of light scatter caused by the blue-sensitive emulsion layer. A further object is to provide a novel multi-layer photographic film.

These objects are accomplished by coating the blue-sensitive layer adjacent the support and including in one of the layers over the blue-sensitive layer a dye or pigment which absorbs light to which one or both of the upper layers are sensitive, particularly a dye or pigment having a transmission in the visible spectral region for blue light only.

The accompanying drawings show in sectional view 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 a blue-sensitive silver halide emulsion layer coated thereon. This is followed by green-sensitive and red-sensitive silver halide emulsion layers either of which may be outermost, although we prefer to coat the green-sensitive or outermost. Since the green-sensitive and red-sensitive silver halide emulsions are sensitive to blue or violet light in addition to the regions to which they are optically sensitive, it is necessary to use a blue light filter on these layers. This may be accomplished either by using as the bottom layer a blue-sensitive emulsion which has much higher blue light speed than the green-sensitive and red-sensitive emulsions and exposing the entire film through a yellow filter which absorbs all blue light to which the upper layers are sensitive but not all blue light to which the bottom layer is sensitive, or by using the thin blue-sensitive emulsions consisting principally of silver chloride, which has very little sensitivity in the visible blue light region. The emulsion layers may contain couplers incorporated, as described in Jelley and Vittum U. S. Patent 2,322,027.

According to the preferred embodiment of our invention, the blue-sensitive layer is a silver bromide or silver chlorobromide emulsion sensitive to visible blue light and containing a coupler capable of forming a blue dye image. The red-sensitive and green-sensitive emulsions are silver chloride or silver chlorobromide emulsions relatively insensitive to visible light and containing, respectively, couplers capable of producing cyan and magenta dye images.

A dye or pigment which absorbs red or green light or both is incorporated in at least one of the layers over the blue-sensitive emulsion layer. This dye or pigment is blue, cyan, magenta or red and is incorporated in the red-sensitive or green-sensitive layers or both or in an inter-layer between these layers and the blue-sensitive layer or a combination of both.

A suitable blue transmitting pigment for this purpose is Prussian Blue or one of the related ferric-ferrocyanides. The following example describes the preparation of inter-layers and emulsions containing Prussian Blue.

Turnbull's Blue in gelatine was prepared by adding simultaneously to 180 cc. of a solution of gelatin in water containing 4.0 grams of gelatin per 100 cc. of water at pH 2.5 to 3.0, a solution of 3.6 grams of ferrous amionium sulfate in 36 cc. of water and a solution of 3.0 grams of potassium ferrocyanide in 36 cc. of water at 40° C. The solutions were run in slowly over a period of three minutes with continuous mechanical stirring.

The dispersion was chilled until the gelatin was entirely set, then chilled and washed in running water for three hours to remove soluble by-products and excess potassium ferrocyanide. This method of precipitation gives a better dispersion than adding the full amount of either of the salts to the gelatin before the other, and the excess ferrocyanide is washed out of the gelatin more readily than excess ferrous salt. Precipitation of a ferric salt by ferrocyanide may also be used under similar conditions allowing one to secure a good dispersion with the method described.

This dispersion may be coated either as an interlayer above the blue-sensitive emulsion or may be mixed directly with the red-sensitive gelatin coating to obtain an inter-layer made in this way when coated at 40 cc. per square meter had an optical density of 1.0 at 690 millimicrons.

This gives adequate protection against scattered light.

During the color processing of a multi-layer film containing Prussian Blue incorporated in an inter-layer or in an emulsion layer or both, the Prussian Blue is bleached in the strongly alkaline developer with the formation of ferric hydroxide and a soluble ferrocyanide. These products are known to be the same whether the precipitate is formed from a ferric salt and ferrocyanide or from a ferrous salt and ferrocyanide. If the film is washed after development, the ferrocyanide will be removed by a subsequent acid bath, which will dissolve the ferric hydroxide. If, however, the film goes directly from the developer into an acid stop bath or fixing bath, there is danger that some Prussian Blue may be reformed. This may be prevented by incorporating in the developer, materials forming complexes with ferric ions such as citrates, tartrates, oxalates, fluorides or ethylene diamine tetraacetic acid. In practice, this has not been found necessary when using an acid dichromate bleach and removal of silver after color development but if a ferrocyanide bleach were employed, precautions for removal of the ferric salts would be necessary.

Besides Prussian Blue, the following dyes and pigments may be used:

1. 2,3,5,3'-tetrphenyl-1,1' - pyrococinolcarbocyanine.
it may be employed either as a dispersion prepared by adding a methanol solution of the dye to gelatin or by adding it to a very fine ground silver bromide light sensitive emulsion to reduce diffusion. The density at 690 m\(\mu\) will be approximately 0.3 for 20 mg. of dye per square meter.

2. In camera films where bleaching of the filter layer is not essential, it is possible to use a dispersion of copper phthalocyanine in gelatin, for example the material sold by Du Pont as Monastral Blue GSWD. This is completely stable against bleaching by ultraviolet light.

3. Bis(1,3-diethyl-2-hydroxybarbituric acid - (S)-1-pentamethineoxonol may be used as a red absorber. For example, to 434 g. of gelatin made up as a 10% solution, there is added 12 g. of Bis(1,3-diethyl-2-hydroxybarbituric acid-(S)-pentamethineoxonol dissolved in 50 cc. pyridine and 1500 cc. methanol. Then 48 g. of polyvinyl pyridine metho-p-toluene-sulfonate dissolved in water are added.

4. A 30 mg. of dye per square meter, the optical density will be approximately 0.3 at the maximum. The dye is described in Gaspar U. S. Patent 2,774,782 and the polyvinyl pyridine mordant in Sprague and Brooker U. S. patent application Serial No. 719,623, filed December 31, 1946.

4. To 454 g. of gelatin as a 10% solution, there are added 3 g. of (4-(3-ethyl-2-(3-benzoxazolylthiocarbonyl)benzenesulfonyl)phenyl-5-pyrazolone dissolved in 200 cc. methanol, 2.5 cc. pyridine and 200 cc. water; then 8 g. of pyridine pyridine metho-p-toluene-sulfonate in 700 cc. of water. Coating at 30 mg. of dye per square meter, the optical density at 550 m\(\mu\) will be approximately 0.3. This dye is prepared in the manner described in Brooker and White U. S. patent application Serial No. 605,472, filed July 16, 1945.

In addition to blue dye or pigment, the film may contain a magenta or reddish dye or pigment. For example, the disodium salt of aurin tetrachloride acid may be incorporated in the layer containing the blue dye or pigment, or in a separate layer.

Our invention will now be described by reference to the accompanying drawings. As shown in Fig. 1 thereof, 10 is a support having thereon a blue-sensitive silver bromide emulsion layer 11, a green-sensitive silver chloride emulsion layer 12 containing a blue dye, and a red-sensitive silver chloride emulsion layer 13.

Fig. 2 illustrates a modification of our invention in which neither the green-sensitive silver chloride emulsion layer 13 nor the red-sensitive silver chloride emulsion layer 14 contains a dye or pigment but a blue pigment is contained in the interlayer 15 between the blue-sensitive emulsion layer 11 and the red-sensitive emulsion layer 14.

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 claims.

We claim:

1. A multi-layer photographic element capable of producing colored images having improved definition, comprising a single support having on one side thereof three, integrally united, silver halide emulsion layers separately sensitive to the blue, green and red spectral regions, said blue-sensitive emulsion layer being adjacent said support and having a much higher blue speed than said green-sensitive and red-sensitive emulsions, and in a layer between said blue-sensitive emulsion layer and the layer farthest from said support, a non-image-forming coloring material absorbing a major amount of red light and a minor amount of green light and transmitting substantially all blue light, said layers being otherwise uncolored with an image-forming coloring material.

2. A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof three silver halide emulsion layers sensitive in the blue, red and green spectral regions, said blue-sensitive emulsion layer being adjacent said support and an insensitive interlayer between said blue-sensitive emulsion layer and said red-sensitive emulsion layer containing a blue coloring material absorbing a major amount of green light and a minor amount of red light and substantially all blue light.

3. A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof three silver halide emulsion layers sensitive in the blue, red and green spectral regions, said blue-sensitive emulsion layer being adjacent said support, and an insensitive interlayer between said blue-sensitive emulsion layer and said red-sensitive emulsion layer containing a blue coloring material absorbing a major amount of green light and transmitting substantially all blue light.

4. A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof three silver halide emulsion layers sensitive in the blue, red and green spectral regions, said blue-sensitive emulsion layer being adjacent said support, said blue-sensitive emulsion layer containing a blue coloring material absorbing a major amount of red light and a minor amount of green light and transmitting substantially all blue light, said layers being otherwise uncolored with an image-forming coloring material.

5. A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof three silver halide emulsion layers sensitive in the blue, red and green spectral regions, said blue-sensitive emulsion layer being adjacent said support, said red-sensitive emulsion layer containing Prussian Blue pigment, said layers being otherwise uncolored with an image-forming coloring material.

6. A multi-layer photographic element capable of producing colored images having improved definition, comprising a support having on one side thereof three silver halide emulsion layers sensitive in the blue, red and green spectral regions, said blue-sensitive emulsion layer being adjacent said support, and in at least a layer other than said blue-sensitive emulsion layer a non-image-forming Prussian Blue pigment, said layers being otherwise uncolored with an image-forming coloring material.

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