April 29, 1941. B. H. CARROLL 2,239,698

PHOTOGRAPHIC ELEMENT

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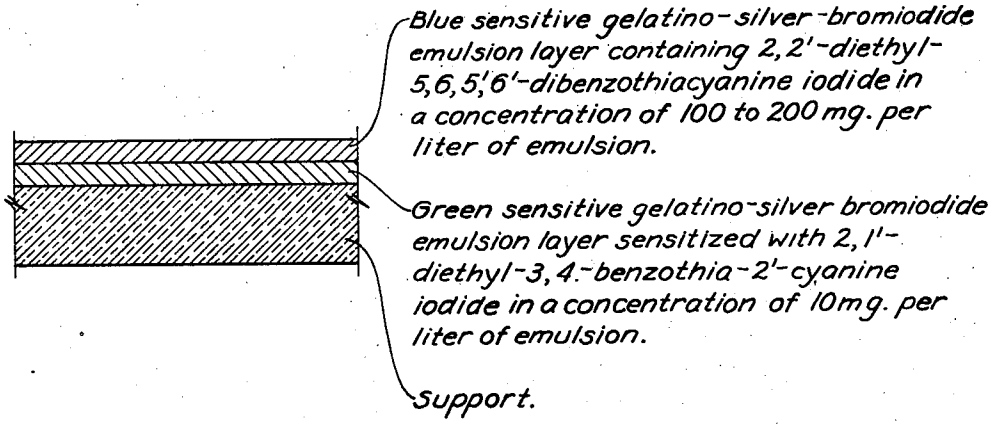

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PHOTOGRAPHIC ELEMENT

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This invention relates to photographic elements and more particularly to photographic elements having two or more silver halide emulsions coated on a single support.

Whenever two or more silver halide emulsion layers of different spectral (color) sensitivity are superposed on a support (whether the layers are separated by an inert colloidal layer or not), as in monopack color processes, one of the principal difficulties encountered is the diffusion of sensitizing dyes from one layer to another. Diffusion becomes very noticeable when an ordinary blue sensitive silver bromide emulsion layer is superposed on a silver halide emulsion layer which is sensitized to green light by means of sensitizing dyes, the sensitizing dyes in the green sensitive layer diffusing into the blue sensitive layer.

I have now found that diffusion of sensitizing dyes from a green sensitive silver bromide (including bromiodide) emulsion layer to an ordinary blue sensitive silver bromide (including bromiodide) emulsion layer superposed thereon, can be prevented by incorporating in the ordinary blue sensitive layer, dyes which adsorb to the silver halide in the layer and impart substantially no extension to the spectral sensitivity of the layer (i. e. impart at most an extension of not more than about twenty millimicrons) in the direction of the longer wavelengths of light.

It is, accordingly, an object of my invention to provide a new photographic element. A further object is to provide a process for preparing such elements. Other objects will become apparent hereinafter.

As dyes which I incorporate in the blue sensitive layer, I have found that certain of those of the cyanine, merocyanine, hemicyanine and hemioxonol classes of dyes are advantageously employed. All of these dyes adsorb to the silver halide in the emulsion layer and certain of the simpler dyes of each class do not extend substantially the sensitivity of silver bromide emulsions, although these same simpler dyes do extend the sensitivity of silver chloride emulsions.

The quantity of dye which is incorporated in the blue-sensitive emulsion layer can vary widely, as even rather small concentrations, e. g. 50 mg. per gram-mole of silver halide in the emulsion, has a beneficial effect. However, to secure practical effects, I have found that the dye-adsorptive capacity of the silver halide in the blue-sensitive emulsion layer is advantageously practically saturated. Ordinarily, from about 400 to about 800 mg. of dye per gram-mole of silver halide in the emulsion layer is necessary to saturate the adsorptive capacity of the silver halide. Exceeding the adsorptive capacity of the silver halide should be avoided, since the blue sensitivity of the silver halide may be depressed, when excesses of the dye are employed. Deleterious excesses of the dye can be detected by observing the presence of free (unadsorbed) dye in the emulsion and by marked depression of the sensitivity of the emulsion. The proper amount of dye will vary from dye to dye and emulsion to emulsion, so that a simple observation should be made before entering upon the use of any particular dye.

The following illustrations will serve to demonstrate the manner of practicing my invention. These illustrations are not intended to limit my invention.

Example

A sufficient amount of a methyl alcoholic solution of 2,2'-diethyl-5,6,5',6'-dibenzothiacyanine iodide was added to an ordinary gelatino-silver-bromiodide emulsion (containing about 0.25 gram-mole of silver halide per liter of emulsion) to give a concentration of cyanine iodide of from 100 to 200 mg. per liter of emulsion. The resulting emulsion was coated upon a gelatino-silver-bromiodide emulsion layer which had been sensitized for the green with 2,1'-diethyl-3,4-benzothia-2'-cyanine iodide in a concentration of about 10 mg. per liter of emulsion, the green-sensitive layer being superimposed on a red-sensitive emulsion layer (sensitized with 2,2'-diethyloxadicarbocyanine iodide) which rests on a suitable support of cellulose acetate film, cellulose nitrate film, polyvinyl acetal resin film, glass or paper. This gives an upper emulsion layer in which the blue sensitivity is only slightly decreased and slightly extended toward the longer wave-lengths, while sensitization by diffusion from the under green-sensitive layer is practically completely eliminated.

Instead of coating the foregoing blue-sensitive emulsion containing the 100 to 200 mg. of cyanine iodide directly upon the green-sensitive emulsion layer, the green sensitive layer can, if desired, first be coated with an inert layer of gelatin which may contain a suitable yellow dye as a filter, and then the blue-sensitive emulsion can be coated on the inert layer..

Instead of the 2,2'-diethyl-5,6,5',6'-dibenzothiacyanine iodide, employed in the foregoing example, 100 to 200 mg. of any of the following dyes can be employed: 2,2'-diethyl-3,4,3',4'-dibenzothiacyanine iodide, 5-(1-methyl-2(1)-β-naphthoxazolylidene)-3-ethylrhodanine, 1-[β-(1-piperidyl) vinyl]-benzothiazole ethiodide.

Such photographic elements as those illustrated above can be employed in color photographic processes, such as described in United States Patent 2,113,329, dated April 5, 1938, for example.

As is well known, in photographic elements containing more than two emulsion layers coated on a single support, the green-sensitive layer can be coated on one side of a support with the blue-sensitive layer superposed thereon, while the red-sensitive layer is coated on the opposite side of the support (or on a separate support), instead of superposing all three layers on one side of a support.

The accompanying drawing shows, diagrammatically, a photographic element, prepared in accordance with one embodiment of my invention, comprising a support coated with a green-sensitive gelatino-silver-bromiodide emulsion layer which is sensitized with 2,1'-diethyl-3,4-benzothia-2'-cyanine iodide, in a concentration of 10 mg. per liter of emulsion, the green-sensitive emulsion layer being coated with a blue-sensitive gelatino-silver-bromiodide layer containing 2,2'-diethyl-5,6,5',6'-dibenzothiacyanine iodide, in a concentration of from 100 to 200 mg. per liter of emulsion.

My invention is, of course, directed primarily to photographic elements made up employing the customary gelatino-silver-bromide (including bromiodide) developing-out emulsions. However, silver bromide emulsions where the carrier is a substance other than gelatin, e. g. a cellulose derivative or resinous material, can also be employed.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A photographic element comprising two silver bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue-sensitive and containing a dye which adsorbs to the silver halide in the layer and imparts substantially no extension to the spectral sensitivity of the layer.

2. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue sensitive and containing a dye which adsorbs to the silver halide in the layer and imparts substantially no extension to the spectral sensitivity of the layer.

3. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue sensitive and containing, in a concentration of at least 50 milligrams per gram-mole of silver halide in the layer, a dye which adsorbs to the silver halide in the layer and imparts substantially no extension to the spectral sensitivity of the layer.

4. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue sensitive and containing, in a concentration of from about 400 milligrams to about 800 milligrams per gram-mole of silver halide in the layer, a dye which adsorbs to the silver halide in the layer and imparts substantially no extension to the spectral sensitivity of the layer.

5. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue sensitive and containing, in a concentration of from about 400 milligrams to about 800 milligrams per gram-mole of silver halide in the layer, a 2,2'-diethyl-dibenzothiacyanine salt.

6. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue-sensitive and containing, in a concentration of from about 400 milligrams to about 800 milligrams per gram-mole of silver halide in the layer, 5-(1-methyl-2(1)-β-naphthoxazolylidene)-3-ethylrhodanine.

7. A photographic element comprising two gelatino-silver-bromide emulsion layers superposed on one side of a support, the one layer being sensitized to green light with a sensitizing dye, and the other layer being blue sensitive and containing, in a concentration of from about 400 milligrams to about 800 milligrams per gram-mole of silver halide in the layer, a 1-[β-(1-piperidyl)-vinyl]-benzothiazole ethyl salt.

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