

Jan. 2, 1973

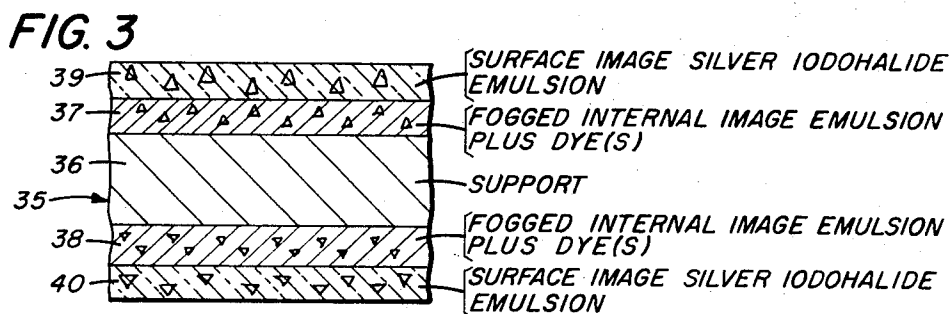
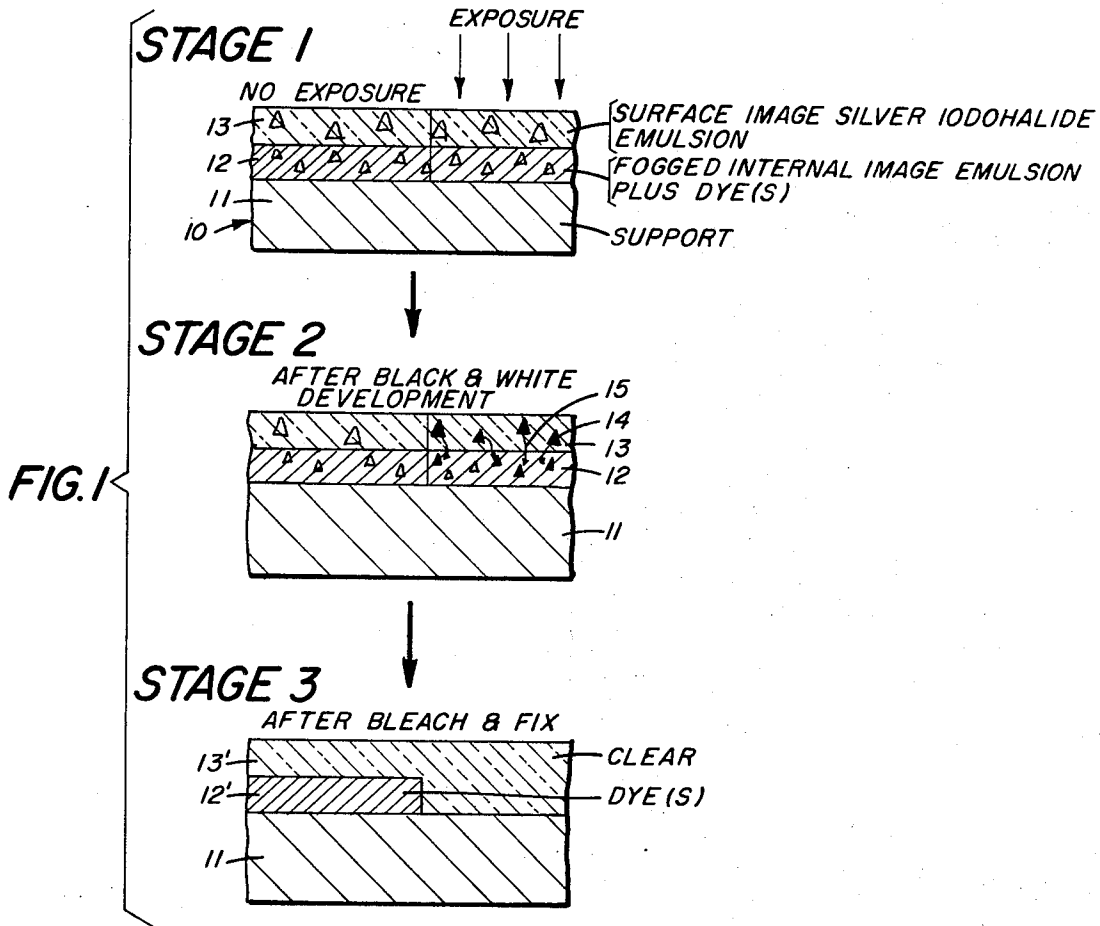
G. W. LUCKEY

3,708,300

SILVER-DYE-BLEACH PHOTOGRAPHIC MATERIALS

Filed Nov. 19, 1970

2 Sheets-Sheet 1



GEORGE W. LUCKEY
INVENTOR.

BY *Remus W. DeLeo*

ATTORNEY

Jan. 2, 1973

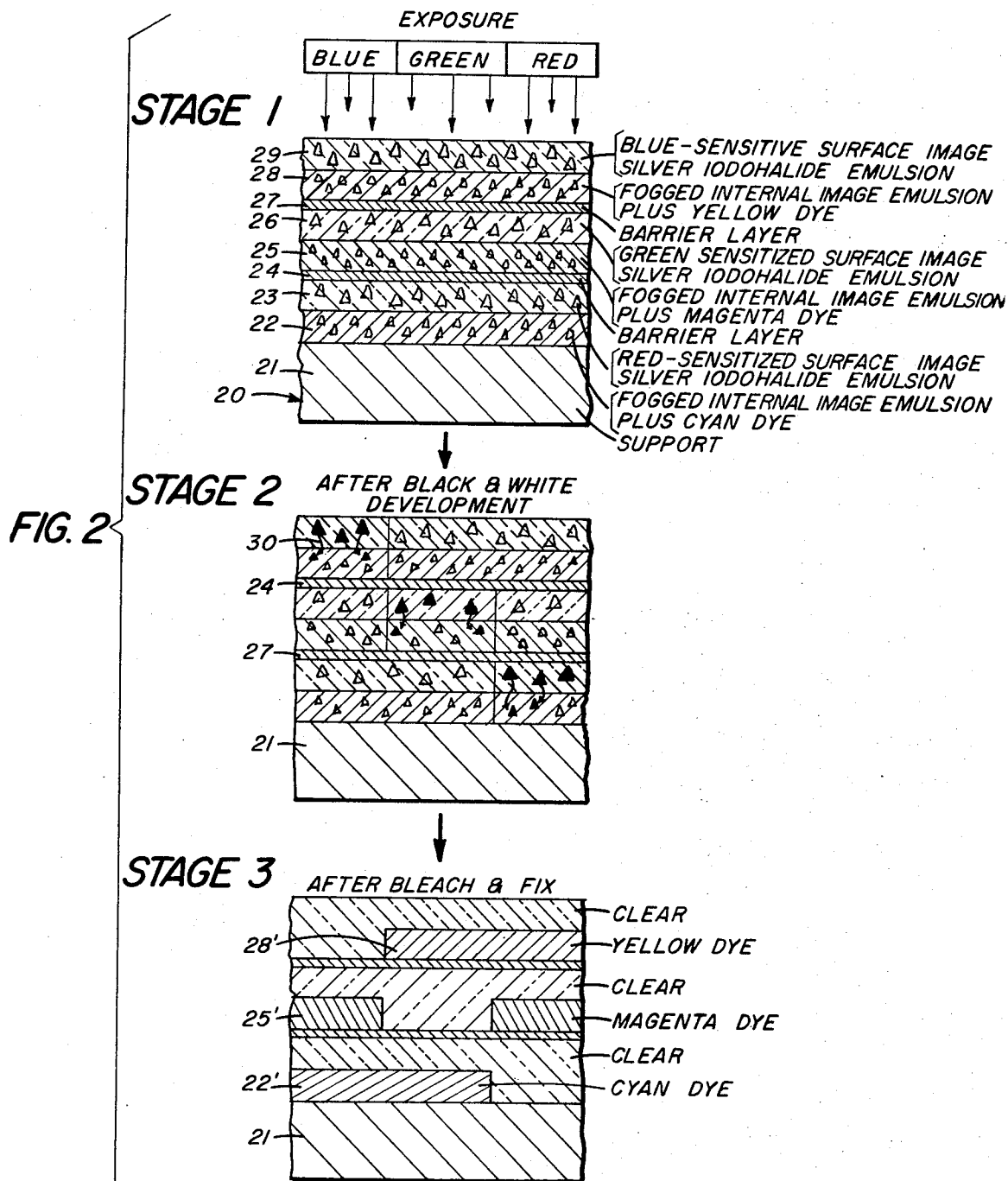
G. W. LUCKEY

3,708,300

SILVER-DYE-BLEACH PHOTOGRAPHIC MATERIALS

Filed Nov. 19, 1970

2 Sheets-Sheet 2



GEORGE W. LUCKEY
INVENTOR.

BY

Deunth. De Leo

ATTORNEY

1

3,708,300

SILVER-DYE-BLEACH PHOTOGRAPHIC MATERIALS

George W. Luckey, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y.

Filed Nov. 19, 1970, Ser. No. 90,928

Int. Cl. G03c 1/76

U.S. Cl. 96—73

10 Claims

ABSTRACT OF THE DISCLOSURE

Silver-dye-bleach photographic elements are prepared by incorporating the image-forming dyes in a fogged internal image silver halide emulsion and coating over this emulsion a layer of unfogged surface-sensitive silver iodohalide emulsion. The dye layer is thus separated from the sensitive layer with consequent improvement in speed and contrast. Upon development of the exposed element, iodide ion released from the silver iodohalide emulsion migrates to the adjacent fogged internal image emulsion and uncovers the internal fog centers, thus permitting their development. Then, upon silver-dye-bleach processing, a positive dye image is obtained which has ample density and contrast.

This invention relates to photography and more particularly to novel photographic silver-dye-bleach materials.

The production of images by the silver-dye-bleach process is based on the use of a photographic element comprising one or more silver halide emulsion layers, each of which contains a bleachable dye of a color complementary to the portion of the spectrum to which its silver halide layer is sensitive. The element is exposed, developed and subsequently treated in a bleach bath wherein the dyes are rendered colorless in proportion to the metallic silver produced during development. After removal of the residual silver and silver halide by silver bleaching, fixing and washing, a positive dye image is obtained.

The conventional silver-dye-bleach process suffers from the disadvantage that the dyes incorporated in the light-sensitive layers absorb a sufficient amount of the exposing light to reduce the effective speed of the photographic element. Various proposals have been made to overcome this disadvantage. One has been to replace the dyes by colorless dye precursors such as nitroso compounds or azo couplers. Another has been to use special azo dyes which have different colors depending on the pH of the medium. During exposure, the pH-sensitive dyes are of a color which will not excessively absorb light to which the layer containing the dyes or the underlying layers are sensitive. Then after exposure, the pH of the element is adjusted to change the dye to the desired color. These procedures have the disadvantage that an additional processing step is needed to convert the dyes or precursors to dyes of the desired hue for the finished image and also the disadvantage that the choice of dyes is limited to those that undergo the desired color shifts.

There is, therefore, a need for improved silver-dye-bleach materials. It is an object of this invention to provide such improved photographic silver-dye-bleach materials. Another object is to provide a novel photographic silver-dye-bleach element having improved light sensitivity, contrast, density and/or stability. It is a further object of the invention to provide such a novel photographic element which can use stable dyes of conventional silver-dye-bleach photography and can be processed by conventional silver-dye-bleach methods without additional processing steps. Still another object is to provide novel silver-dye-bleach photographic elements in which the

2

bleachable dye or dyes are positioned in a separate layer contiguous to the light-sensitive layer, with consequent improvement in speed, contrast and/or stability and such elements that are especially adapted for color photography or radiography. These and other objects and advantages of the present invention will be apparent from the description herein.

The present invention is based on my discovery that silver-dye-bleach photographic materials having marked improvement in speed and other advantages over conventional silver-dye-bleach materials can be obtained by incorporating the bleachable dyes in a fogged internal latent image silver halide emulsion which is overcoated with an unfogged surface image silver iodohalide emulsion.

The novel photographic elements in the invention thus, in general, comprise a support, a fogged silver halide emulsion layer of internal latent image silver halide grains and, in close proximity, for example, contiguous or adjacent thereto, an unfogged emulsion layer of surface latent image silver iodohalide grains, the fogged emulsion layer containing a dye which is bleachable in the presence of developed silver.

In a photographic element of the invention which is intended for photographic exposure from the top the fogged emulsion layer is positioned between the support and the unfogged surface-sensitive emulsion layer. However, photographic elements which are intended for photographic exposure through their transparent support are also within the scope of the invention. For such elements the unfogged surface-sensitive emulsion layer is positioned between the support and the fogged emulsion layer.

One embodiment of the invention, which is adapted for color photography, comprises a support and at least three pairs of said first and second emulsion layers. These are coated sequentially over the support and comprise, in the direction from the support to the upper surface of the element, (1) an emulsion layer of fogged internal latent image silver halide grains containing a cyan dye which is bleachable in the presence of developed silver, (2) a red-sensitized emulsion layer of unfogged surface latent image silver iodohalide grains, (3) an emulsion layer of fogged internal latent image silver halide grains containing a magenta dye which is bleachable in the presence of developed silver, (4) a green-sensitized emulsion layer of unfogged surface latent image silver iodohalide grains, (5) an emulsion layer of fogged internal latent image silver halide grains containing a yellow dye which is bleachable in the presence of developed silver, and (6) a blue-sensitive emulsion layer of unfogged surface latent image silver iodohalide grains. In certain of these multi-layer embodiments, the fogged internal latent image grains are protected by mercapto development antifoggants and the migration of iodide ion between layers is controlled by the barrier interlayers.

The described sequence of layers is especially adapted for color photographic elements intended for photographic exposure from the top. It should be understood, however, that the relative positions of the fogged and unfogged layers within each pair of layers can be reversed, as mentioned above, and the sequence of color-sensitivities can be different, for example, with the blue-sensitive layer being closest to the support when the element is designed for exposure through the base.

Another embodiment of the invention, which is particularly useful for radiography, comprises a support having coated on each side thereof an emulsion layer of fogged internal latent image silver halide grains and coated over each of said layers an emulsion layer of unfogged surface latent image silver iodohalide grains, each of the first emulsion layers containing a dye or mixture of dyes which are bleachable in the presence of developed silver.

As background for understanding the types of emulsions employed in the novel photographic elements, it can be explained that silver halide grains employed in photographic emulsions have both surface and internal sensitivity to light. These types of sensitivity can vary considerably among different emulsions, and the silver halide crystals having a high ratio of surface-to-internal sensitivity are used in most photographic emulsions, the latter being referred to as surface latent image emulsions or surface-sensitive emulsions.

Silver halide grains having a high ratio of internal-to-surface sensitivity are also well-known but are less generally employed. Emulsions of such grains, which are referred to as internal latent image emulsions, are described, for example, in Mees, "The Theory of the Photographic Process," p. 221, Revised Edition (1954) and Chapter 6, Third Edition (1966); "Journal of the Optical Society of America," 31, 385 (1941); and Davey et al. U.S. Pat. 2,592,250 of Apr. 8, 1952.

Although I do not wish to be bound by theoretical explanations of the mechanism, it appears that the results obtained with the novel photographic elements occur, at least in part, because a product or products from the development of the surface latent image-bearing emulsion grains migrate to some of the nearly internally prefogged emulsion grains and there uncover the internal fog centers, thus permitting the development of these grains, the production of silver and the consequent bleaching of associated dye. These effects are observed in silver iodohalide surface sensitive emulsions such as ordinary silver bromiodide emulsions. It appears that the important product of the development of such emulsions which migrates to the internal latent image emulsion is the iodide ion.

The invention will be described in more detail by reference to the drawings of which:

FIG. 1 is an enlarged diagrammatic cross section of a monochrome photographic element of the invention shown in different stages of exposure and processing.

FIG. 2 is an enlarged diagrammatic cross section of a multilayer color photographic element of the invention shown in different stages of exposure and processing.

FIG. 3 is an enlarged diagrammatic cross section of still another embodiment of the invention which is adapted for use in radiography.

Referring to Stage 1 of FIG. 1, element 10 is a photographic element of the present invention adapted for black-and-white or monochrome photography which comprises a support 11 on which is coated a fogged internal image emulsion layer 12. This emulsion contains a dye of any desired color which is bleachable under silver-dye-bleach processing conditions, or contains a bleachable mixture of dyes which advantageously produce a neutral image. In close proximity to the emulsion layer 12, and, more particularly, coated over it as an adjacent or contiguous layer is an unfogged silver bromiodide surface-sensitive emulsion 13. There can also be other conventional layers, not shown in the drawing, such as an antihalation layer on support 11, a subbing layer between support 11 and emulsion layer 12 to improve adhesion, a protective gelatin overcoat above emulsion layer 13 or any other suitable layers.

Following the exposure indicated as Stage 1 of FIG. 1, the photographic element 10 is developed, e.g., in a conventional black-and-white developer solution. Stage 2 of FIG. 1 illustrates schematically the postulated result of this treatment. It shows the relatively large, developed silver iodohalide grains 14 of emulsion layer 13 from which the release iodide ions are migrating (as represented by arrows 15) to the vicinity of the prefogged, relatively fine, internal latent image silver halide grains of layer 12. Here the iodide ions apparently act to uncover the internal fog centers and permit the development of these grains in a highly efficient manner. Located close to these developed grains in the emulsion layer 12 is a dye which

is bleachable in the presence of developed silver, or if desired a mixture of such dyes, for example, a mixture that yields a neutral image. Since the dye or dyes are located near the reduced silver of the internal image emulsion and since this reduced silver is finely divided, because of the small grain size of the emulsion and the high level of pre-exposure, the efficiency of dye bleaching is greatly improved and the speed of processing is increased.

Stage 3 of FIG. 1 illustrates the appearance of the cross section of element 10 following bleaching of the element with a suitable silver-dye bleach material and after fixing with a solution of thiosulfate or other fixing agent. It will be noted that the area 13' which includes the entire area of emulsion layer 13 and the exposed portion of emulsion layer 12 is now clear. The silver halide in these areas has been removed by the fixing agent and the dye and the metallic silver in the exposed portion of emulsion layer 12 have been bleached. The non-exposed area 12' of emulsion layer 12 remains dyed.

The embodiment of FIG. 1 is a relatively simple form of the novel silver-dye-bleach photographic element, but the invention extends to other embodiments, including multilayer elements for color photography, as illustrated in FIG. 2, and radiographic elements as illustrated in FIG. 3. Before proceeding with a discussion of these other figures, it will be advantageous to discuss emulsion compositions and the like that are relevant to various embodiments of the invention.

The surface image emulsions useful in the photographic elements of my invention comprise those which, when measured according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing the test portion to a light intensity scale for a fixed time between 0.01 and 1 second and development for 6 minutes at 68° F. in Developer A as hereinafter defined, have a sensitivity, measured at a density of 0.1 above fog, greater than the sensitivity of an identical test portion of the same emulsion which has been exposed in the same way, bleached 5 minutes in aqueous 0.3 percent potassium ferricyanide solution at 65° F., and developed for 5 minutes at 65° F. in Developer B as hereinafter defined. Developer A is the usual type of surface image developer and Developer B is an internal developer having high silver halide solvent activity.

The degree of internal sensitivity of the surface image emulsion is not critical. It can have relatively little or a fair amount of internal sensitivity, but preferably the internal sensitivity is not greater than the surface activity.

The iodide-containing surface sensitive emulsions are referred to herein as silver iodohalide emulsions.

The term silver iodohalide is used in the broad sense to include all iodide-containing photographic silver halides, such as, for example, silver iodide, silver bromiodide, silver chloriodide, silver chlorobromiodide, and the like, the preferred halide being bromiodide. The halide content of the surface sensitive silver iodohalide emulsion comprises from about 0.5 to 100 mole percent iodide and preferably from 5 to 30 mole percent iodide.

Suitable surface image silver iodohalide emulsions can be prepared by the method described by Trivelli and Smith in "The Photographic Journal," volume LXXX, July 1940 (pages 285-288).

The surface image emulsions can have high or low contrast, and useful effects have been obtained with both types of emulsions. The surface image emulsions useful in my invention can also be characterized as having a D_{max} greater than about 0.50 when the emulsion is coated at a coverage of about 540 mg. of silver per square foot, exposed to a stepwedge and processed for 12 minutes in Developer C as hereinafter defined.

The internal image emulsion useful in my novel photographic element, such as the emulsion of layer 12 in FIG. 1, is one which, when measured according to nor-

mal photographic techniques in its unfogged stage by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale having a fixed time between 0.01 and 1 second, bleaching 5 minutes in a 0.3% potassium ferricyanide solution at 65° F. and developing for about 5 minutes at 65° F. in Developer B, has a sensitivity, measured at a density of 0.1 above fog, appreciably greater (e.g., at least 1.4 log E greater) than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68° F. in Developer A. Several suitable emulsions of this type are described in Davey and Knott U.S. Pat. 2,592,250, issued Apr. 8, 1952. Any of the photographic silver halides can be used in the internal image emulsions such as silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide crystals or mixtures thereof.

The internal image emulsions must be fogged, partly or completely, before use. The fogging should be sufficient to give a density of at least 0.50 when one mole (AgX) of the fogged emulsion is coated in a blend with 3 moles of surface image emulsion at a total coverage of about 540 mg. of silver per square foot and processed for 5 minutes in Developer B. The D_{max} of the unfogged internal image emulsions should be less than about 0.30 when the emulsions are exposed to D_{max} and processed for 8 minutes in Developer C, as identified hereinafter.

The fogging of the internal image emulsions can be effected by merely exposing the emulsions to light; or other methods, such as chemical fogging, can be used. The emulsions having high internal fog but low surface sensitivity can be prepared by fogging an emulsion having both internal and surface sensitivity and then bleaching the surface image with a solution of potassium ferricyanide. Another way of obtaining the fogged internal image emulsions is by exposure of non-fogged internal image emulsions to high energy radiation, such as X-rays.

It is also advantageous to employ internal image emulsions in the novel photographic elements which have been treated with development antifoggants, including mercapto antifoggants such as 1-phenyl-5-mercaptotetrazole and related compounds as disclosed in Luckey et al. U.S. Pat. 3,397,987.

The molar ratio of silver content of the surface latent image emulsion layer to that of the fogged internal image emulsion layer can be varied over a wide range, depending upon such factors as the types of emulsions used, the contrast of the emulsions and the dye density desired. For instance, molar ratios based on silver content of the surface image emulsion to that of the fogged internal image emulsion over a range of 42:1 to 1:10 or even over a broader range are feasible, although preferably the ratio is in the range from about 5:1 to 1:5.

The emulsion combinations described herein can be processed in developers containing silver halide solvents such as potassium thiocyanate (KSCN), sodium sulfite, etc., as well as in developers having little or no silver halide solvent activity. However, the silver halide solvent action of the developer should not be too high because iodide would be released indiscriminantly from the iodide-containing surface image emulsion and the fogged internal image emulsion would become spontaneously developable, resulting in overall dye bleaching. If an appropriate amount of silver halide solvent, such as a water-soluble thiocyanate, thiosulfate, sodium sulfite or the like, is used in the developer the fogged internal image emulsion then develops only in the areas where the exposed surface image grains develop, resulting in the improvements illustrated in my invention.

Without being bound by theoretical explanations, a comment can be made on the effect of silver halide solvent and of iodide ion in the developer as illustrated in Examples 12 and 13 hereinafter. The effect of these possible additives can be explained in terms of the threshold iodide concentration required for development of

the prefogged internal latent image emulsion. It appears that a minimum or threshold iodide concentration must be reached before the prefogged internal latent image grains can be developed. The iodide ion concentration in the region of these grains can be just below this threshold limit and no development of the latent fog centers occurs until the threshold is at least slightly exceeded. To improve the sensitivity of the photographic elements of the invention, therefore, it is sometimes desirable to provide an iodide ion concentration somewhat below the threshold limit throughout the internal image emulsion. Then, as iodide ions from the developed exposed areas of the surface sensitive emulsion migrate to the adjacent internal image emulsion, only a small concentration of migrating iodide ion is required to exceed the threshold limit and promote the development of the prefogged internal latent image emulsion in a pattern corresponding to the exposure of the surface sensitive emulsion.

The concentration of iodide ion below the threshold limit can be provided in several ways. Thus the developer can contain iodide ion in an amount just below that which provides the threshold concentration for the internal image emulsion. Likewise, silver halide solvent in the developer solution by its solvent action can cause the transfer of silver iodide from the iodide-containing surface sensitive emulsion to the region of the internal latent emulsion, but again the concentration of silver halide solvent must not be so great as to dissolve enough silver halide to exceed the threshold iodide concentration in the region of the internal latent image emulsion.

These solvents can also cause solution of the grains of the internal image emulsion and permit development of the internal image, particularly if these grains are not protected by antifoggants such as those disclosed in Luckey et al. U.S. Pat. 3,397,987. Accordingly, if the antifoggants are not present in the internal image emulsion the silver halide solvent content of the developer should be correspondingly low.

Still another possibility is to incorporate a source of iodide ion in the photographic element itself. This can be done, for example, by incorporating inorganic iodide such as lead iodide, thallous iodide or silver iodide or an organic iodine complex in a separate layer of the element. The desirable limits of iodide concentration in the developer or in a layer of the photographic element and the limits for silver halide solvent concentration can be determined by routine tests. For instance, a series of test film strips of photographic elements of the invention which differ only in iodide levels can be exposed and processed identically and the maximum iodide level for an image of desired contrast can be determined. Similarly, identical test films can be developed with a series of developer compositions of varying iodide content and/or silver halide solvent content to determine the proper levels for optimum results. These techniques for augmenting the iodide content by adding iodide or silver halide solvent to the developer solution or incorporating a special iodide-releasing layer in the photographic element are mainly useful when the silver iodohalide emulsions are thin, as in multi-layer color elements, or when the silver iodohalide has a low iodide content. With thicker emulsion coatings of higher iodide content there is usually no advantage in providing additional iodide.

To inhibit development fog which can be produced when the iodide content of the developer builds up excessively, as may occur when developer solutions are used for a long time without replenishment, it is advantageous to include in the photographic elements of the invention a fog inhibiting layer as disclosed in French Pat. 2,006,427 of Dec. 26, 1969. This a low-speed emulsion of low-iodide content, e.g., a silver chlorobromide emulsion, which is positioned below the prefogged internal latent image emulsion or over the surface sensitive emulsion.

7

The following developing solutions are examples of solutions that can be used in the processing of the photographic elements described in this application. They are identified below by letters with which they are referred to in the foregoing descriptions of the useful surface sensitive and internal image emulsions.

A

	Grams
N-methyl-p-aminophenol sulfate -----	0.31
Sodium sulfite, desiccated -----	39.6
Hydroquinone -----	6.0
Sodium carbonate, desiccated -----	18.7
Potassium bromide -----	0.86
Citric acid -----	0.68
Potassium metabisulfite -----	1.5
Water to 1 liter.	

B

N-methyl-p-aminophenol sulfate -----	2.0
Sodium sulfite, desiccated -----	90.0
Hydroquinone -----	8.0
Sodium carbonate, monohydrate -----	52.5
Potassium bromide -----	5.0
Sodium thiosulfate -----	10.0
Water to 1 liter.	

C

N-methyl-p-aminophenol sulfate -----	2.5
Sodium sulfite, desiccated -----	30.0
Hydroquinone -----	2.5
Sodium thiosulfate -----	5.0
Potassium bromide -----	0.5
Water to 1 liter.	

FIG. 2 of the drawings illustrates stages in the exposure and processing of a multilayer photographic element of the invention which is adapted for three-color subtractive photography. Referring to Stage 1 of FIG. 2, the element 20 comprises a support 21 such as a cellulose acetate film base, on which is coated a layer 22 of fogged internal image silver halide emulsion in which is dispersed a cyan dye which is bleachable in the presence of developed silver. Above layer 22 is coated a layer 23 of unfogged surface image silver iodohalide emulsion which is sensitized to red light by means of a suitable spectral sensitizing dye.

In these multilayer color materials, the migration of iodide ion and bleach catalyst is advantageously controlled to prevent the development in one pair of emulsions from affecting the grains in another pair. For example, the layer of red-sensitized emulsion and its associated layer of dye and fogged internal image grains are separated from the green-sensitized layer and its associated dye and internal image grains by a barrier that prevents the diffusion of iodide ion and reduced bleach catalyst. A suitable layer of this type is an insensitive, fine grain emulsion, such as a Lippmann emulsion which advantageously may contain a diffusion inhibiting compound such as a ballasted paraquinone, e.g., 2,5-di-n-octyl-p-benzoquinone, or other compound of this type as disclosed, for example, in British Pat. 1,159,690 and U.S. Pat. 3,457,074. Various other materials which serve as barriers to migration of iodide ion or reduced bleach catalyst can also be used.

The barrier layers may also contain filter material such as filter dyes or colloidal silver to prevent exposure of the red- and green-sensitized layers by blue light and to improve the color separation of the system.

Layer 24 of FIG. 2 is a barrier layer of the type described. For example, layer 24 is an insensitive Lippmann emulsion which controls or inhibits the migration of iodide ions between layers 23 and 25.

Above the barrier layer 24 is coated a fogged internal latent image emulsion layer 25 which contains a magenta dye and above it is coated a green-sensitized surface image silver iodohalide emulsion 26. Next is another barrier layer 27, then a fogged internal image emulsion layer 28, which

8

contains a yellow dye and over it is coated a blue-sensitive surface image silver iodohalide emulsion layer 29.

Omitted from the diagrammatic drawing for simplicity are various conventional layers which can be used as desired, such as antihalation and topcoat layers.

Stage 2 of FIG. 1, by means of arrows 30, indicates the migration of iodide ions from the exposed areas of each of the surface-sensitive emulsion layers 29, 26 and 23 to the adjacent fogged internal image layers where they uncover prefogged internal latent image fine grain silver halide grains in a pattern corresponding to that of the exposure and development of the immediately overlying surface-sensitive emulsion layer. Further migration of these iodide ions is blocked by the barrier layers 24 and 27.

After the black-and-white development of the exposed film as shown in Stage 2, FIG. 2, the unreduced silver halide in the various emulsion layers is rendered soluble in a conventional fixing bath and subsequently removed from the film by washing. The film is then placed in a dye-bleach bath in which the dyes in emulsion layers 22, 25 and 28 are destroyed in the areas corresponding to the developed silver images. Finally the film is silver bleached, fixed and washed in order to remove any residual silver and silver salt. The product obtained, shown in Stage 3, has yellow, magenta and cyan positive images in layers 28', and 25' and 22', respectively. A positive three-color reproduction of the original scene is thereby obtained.

FIG. 3 represents a photographic film 35 in accordance with the invention which is intended for use in radiography. It comprises a support 36 having emulsion layers coated on both of its surfaces. Layers 37 and 37 are fogged internal latent image emulsions which contain a bleachable dye or, advantageously, a mixture of such dyes that yields a neutral image. Then adjacent to layers 37 and 38 are coated layers 39 and 40 which comprise surface image silver iodohalide emulsions.

The radiographic or X-ray film 35 can be exposed directly to X-ray or gamma rays or can be used with one or more fluorescent intensifying screens in known manner. In either event, the film is subjected to X-ray or gamma ray exposure and thereafter is developed and subjected to dye-bleach and silver bleach treatments in substantially the same manner as has been described for the processing of the photographic element of FIG. 1.

When used in radiography, the very high covering power that can be obtained with the silver-dye-bleach elements of the invention is particularly advantageous. Other characteristics of the system that are attractive in radiographic as well as other uses include the rapid and simple processing that is possible and the stability of the dyes that can be used. Still another advantage is that the processing can be simplified by photographing the wet positive dye image with a negative microfilm. This combination of a layer of unfogged surface latent image silver iodohalide emulsion and a layer of fogged internal latent image silver halide emulsion-containing dye can also be used for unsharp masking or in combination with other layers to obtain special effects. For example, a positive dye image can be formed on one side of a support and used to mask a negative image on the other side.

Further understanding of the invention is provided by the examples hereinafter which illustrate the compositions of photographic elements of the invention and their use in comparison with other photographic elements. In these examples, the various layers are coated on a polyethylene terephthalate film support having a black dye layer on the back. Examples 7 through 9 represent photographic elements of the present invention, and Examples 1 through 6 and 10 are other photographic elements which are provided for comparison. The coatings of Examples 1 through 9, besides containing a dye as indicated in the examples, also contain a dye mordant, copoly(alpha-methylallyl-N-guanidyl ketimine styrene) glycolic acid salt.

The first three examples represent a conventional type of silver-dye-bleach film in which the azo dye is incorporated in the light-sensitive silver halide emulsion.

9

EXAMPLE 1

The coating consists of an unfogged, coarse grain, high-speed surface-sensitive silver bromiodide gelatin emulsion containing a yellow azo dye. It is coated at 108 mg. Ag/ft.² with 70 mg. of yellow azo dye and 546 mg. of gelatin/ft.².

EXAMPLE 2

The coating consists of the silver bromiodide of Example 1 (108 mg. Ag/ft.²) coated with 52 mg. of magenta azo dye and 496 mg. gelatin/ft.².

EXAMPLE 3

The coating consists of the silver bromiodide of Example 1 (108 mg. Ag/ft.²) coated with 70 mg. of cyan azo dye and 571 mg. gelatin/ft.².

The next three examples represent photographic elements in which the light-sensitive emulsion is coated over a layer of gelatin containing the azo dye.

EXAMPLE 4

The coating consists of the silver bromiodide of Example 1 (108 mg. Ag/ft.²) in 246 mg. gelatin/ft.² coated on top of a layer of 70 mg. of yellow azo dye in 300 mg. gelatin/ft.².

EXAMPLE 5

The coating consists of the silver bromiodide of Example 1 (108 mg. Ag/ft.²) in 246 mg. gelatin/ft.² coated on top of a layer of 52 mg. of magenta azo dye in 250 mg. gelatin/ft.².

EXAMPLE 6

The coating consists of the silver bromiodide of Example 1 (108 mg. Ag/ft.²) in 246 mg. gelatin/ft.² coated on top of a layer of 70 mg. of cyan azo dye in 324 mg. gelatin/ft.².

The next three examples represent photographic elements of the invention in which the unfogged surface-sensitive silver bromiodide emulsion is coated over a layer of fogged internal latent image emulsion containing an azo dye.

EXAMPLE 7

An emulsion of the unfogged silver bromiodide (108 mg. Ag/ft.²) in 246 mg. gelatin/ft.² is coated on top of a layer of a prefogged internal latent image emulsion layer composed of silver chlorobromide (40 mg. Ag/ft.²) in 344 mg. gelatin/ft.² and containing 70 mg. of yellow azo dye.

EXAMPLE 8

A silver bromiodide emulsion as in Example 7 is coated on top of a prefogged internal latent image emulsion layer composed of silver chlorobromide (40 mg. Ag/ft.²) in 294 mg. gelatin/ft.² and containing 52 mg. of magenta azo dye.

EXAMPLE 9

A silver bromiodide emulsion as in Example 7 is coated on top of a prefogged internal latent image emulsion layer composed of silver chlorobromide (40 mg. Ag/ft.²) in 368 mg. gelatin/ft.² and containing 70 mg. of cyan azo dye.

The next example is a comparative example of a photographic element comprising two emulsion layers but containing no dye.

EXAMPLE 10

A layer of 82.5 mg. of gelatin/ft.² is coated on top of a layer of silver bromiodide (450 mg. Ag/ft.²) as in Example 1 in 1025 mg. of gelatin/ft.², which in turn is coated over a layer of prefogged internal latent image silver chlorobromide (164.5 mg. Ag/ft.²) in 181.5 mg. of gelatin/ft.².

The next example describes the exposure and processing of the photographic elements of Examples 1-10.

10

EXAMPLE 11

The coatings are exposed for 1/25 second through a neutral density step tablet with an Eastman Ib sensitometer to a tungsten illuminant filtered by a Kodak Wratten filter No. 47B. After exposure, the coatings are developed at 75° F. for 5 minutes in Developer D (Kodak DK-50 developer solution modified by the addition of 2 grams of the silver halide solvent, potassium thiocyanate, identified hereinafter as KSCN) and 0.05 gram 5-methylbenzotriazole per liter.

The coatings with dye (Examples 1-9) are rinsed in water for 10 seconds, fixed for 3 minutes in Kodak F-5 fixer with hardener at 68° F., then bleached at 90° F. in the following dye-bleach solution, which is hereinafter referred to as Dye-Bleach A.

Thiourea -----g-- 100
37.5 percent hydrochloric acid -----ml-- 200
Acetic acid -----ml-- 15
2-hydroxy-3-amino phenazine -----mg-- 150
Water to 1 liter.

The bleaching times for the nine dye-containing coatings are: Examples 1, 4 and 7: 50 seconds; Examples 2, 5 and 8: 40 seconds; and Examples 3, 6 and 9: 120 seconds.

The 2-hydroxy-3-amino phenazine is dissolved in a mixture of the acetic acid and 15 ml. of water, then added to the solution of thiourea and hydrochloric acid. The coating without dye (Example 10) is rinsed and fixed. All coatings are subsequently rinsed in water and dried in air.

The results of these tests are summarized in the table below:

TABLE I

Example No.	Minimum density	Speed at 0.1 above D _{min.}	Speed at 0.1 below D _{max.} (color)	γ	D _{max.}
10.....	0.15	100	-----	1.9	3.3
1.....	0.22	-----	-----	0.04	0.27
4.....	0.94	-----	43	0.14	1.15
7.....	0.18	-----	155	0.55	0.64
2.....	0.22	-----	22	0.54	1.29
5.....	1.32	-----	57	0.22	1.66
3.....	0.18	-----	145	0.44	0.52
8.....	0.13	-----	23	0.92	1.40
6.....	1.52	-----	58	0.31	2.10
9.....	0.50	-----	85	0.59	1.35

The densities are measured with a Macbeth Quantalog densitometer, Model TD-102. Class A58 blue, green and red filters are used to measure the densities of the yellow, magenta and cyan dyes, respectively.

The data in the table above show that the coatings prepared in accordance with this invention (Examples 7, 8 and 9) have more speed than coatings in which the dye is incorporated in the layer of sensitive emulsion (Examples 1, 2 and 3) and more contrast than coatings in which the dye is placed in a gelatin layer underneath the sensitive emulsion (Examples 4, 5 and 6).

The next example describes exposure of additional samples of the films of Examples 1-10, followed by processing with a developer different from that used in Example 11.

EXAMPLE 12

The coatings of Examples 1-10 were exposed for 1/25 second through a neutral density step tablet with an Eastman Ib sensitometer to a tungsten illuminant filtered by a Kodak Wratten filter No. 47B. After exposure, the coatings were processed in the following manner:

Development in Developer E --- 2 1/2 min., 90° F.
Wash in water ----- 30 sec., 68° F.
Fix in Kodak F-5 Fixer ----- 3 min., 68° F.
Dye Bleach A ----- From 40 to 120 seconds as in Example 11.

Wash in water.
Dry in air.

11

Developer E composition:	Grams
Phenidone ¹ -----	1
Hydroquinone -----	20
Sodium sulfite, anhydrous -----	50
Sodium metaborate, 8H ₂ O -----	22
Potassium bromide -----	15
Potassium iodide -----	0.04
Water to 1 liter, pH 9.6 at 70° F.	

The results of these tests are summarized in Table II below. The densities were measured as described earlier.

TABLE II

Example No.	Minimum density	Speed at 0.1 above D _{min.}	Speed at 0.1 below D _{max.} (color)	γ	D _{max.}
10.-----	0.17	87	1.45	2.85	
1.-----	0.22	-----	16.6	0.26	0.80
4.-----	0.99	-----	62	0.22	1.25
7.-----	0.20	-----	105	0.65	1.02
2.-----	0.21	-----	31	0.69	1.38
5.-----	1.38	-----	58	0.26	1.76
8.-----	0.17	-----	229	1.01	0.96
3.-----	0.10	-----	18	1.22	1.80
6.-----	1.51	-----	58	0.42	2.04
9.-----	0.39	-----	96	0.85	1.72

¹ "Phenidone" is a trademark of Ilford, Ltd., for 1-phenyl-3-pyrazolidone.

The data in Table II indicate that the lower silver halide solvent power of Developer E improves the maximum density and contrast of the dye images without increasing the minimum density. I have also found that removal of iodide ion from Developer E substantially decreases the speed and contrast of the new films and increases the minimum density of the dye image. Thus there is an advantage in the use of additional iodide ion in the developer because of the low coverage of silver iodohalide in the top coating of these two-layer films. If the coverage or iodide content of the sensitive emulsion is increased, the benefits resulting from iodide ion in the developer decrease. However, there is an additional advantage in using iodide ion in the developer; namely, increased stability of the process. The development of the silver iodobromide emulsion releases iodide ion into the developer, and this can cause changes in the sensitometric characteristics of these films as already indicated. By using substantial quantities of iodide ion in the developer, the effects of released iodide are minimized and reliable sensitometric characteristics are obtained.

The next example further illustrates the influence of silver halide solvent in the black-and-white developing solution.

EXAMPLE 13

A photographic element of the invention of the type described in Example 8 was sensitometrically exposed through a graduated density test object and processed using black-and-white development solutions containing varying amounts of silver halide solvent (KSCN). The photographic element consisted of a support on which was coated a prefogged, fine grain internal image silver halide of the type disclosed in U.S. Pat. 2,996,382 and containing 40 mg./ft.² of silver chlorobromide, 294 mg. gelatin/ft.², 52 mg. of magenta azo dye (Solantine Pink 4BL) and 157 mg. of mordant for the magenta azo dye, copoly(alpha-methylallyl - N - guanidyl ketimine-styrene)glycolic acid salt. Coated over this was an emulsion layer of unfogged surface-sensitive silver bromoiodide, (108 mg./ft.²) in gelatin (246 mg./ft.²). The processing steps were as follows:

12

Black-and-white development ¹ -----	min. 2
Wash -----	sec. 30
Kodak F-5 Fix -----	min. 3
Wash -----	min. 5
Ag-Dye-Bleach ² -----	min. 2
Wash -----	min. 1
Cupric bleach ³ -----	min. 2
Kodak F-5 Fix -----	min. 2
Wash -----	min. 5

10	¹ Developer:
	Kodak D-72 type developer ---- 1000 ml.
	KSCN (silver halide solvent) --- Variable (see Table III)
	² Ag-Dye-Bleach:
	HCl ----- ml. 100
	Phenazine (bleach catalyst) ----- g. 0.018
	Thiourea ----- g. 100
15	³ Cupric bleach:
	CuSO ₄ ----- g. 100
	HCl ----- ml. 15.0

The densitometric results tabulated in Table III indicate that image reproduction is improved when some but not too much silver halide solvent is present in the developer.

TABLE III

G. KSCN/l developer	D _{max.}	D _{min.}
0.-----	1.76	0.32
1.-----	1.76	0.04
2.-----	1.70	0.04
4.-----	1.04	0.04

Similarly, improved yellow dye images were obtained by processing silver-dye-bleach elements of the invention containing the yellow azo dye Solantine Yellow RL.

The following examples illustrate another series of photographic elements of the invention, including elements that contain a barrier layer between pairs of emulsion layers.

EXAMPLES 14-20

The photographic elements of this series of examples can be identified with reference to the following basic arrangement of layers. Variations in the basic arrangement for each example are indicated below. The numbers in parentheses in connection with each component of the various layers represents the concentrations in mg./ft.² for each component.

Layer 5....	Blue-sensitive silver bromoiodide gelatin emulsion containing 6 mole percent silver iodide (108), gelatin (246).
Layer 4....	Fogged internal image silver bromide gelatin emulsion (40), gelatin (344), yellow azo dye (70).
Layer 3....	Very fine grain silver bromide (Lippmann-type) emulsion (0), gelatin (200), 2,5-di-n-octyl-p-benzoquinone (14).
Layer 2....	Green-sensitized silver bromoiodide gelatin emulsion containing 6 mole percent silver iodide (108), gelatin (246).
Layer 1....	Fogged internal image silver bromide gelatin emulsion (40), gelatin (294), magenta azo dye (52).
Gelatin (200)	
/// Polyethylene terephthalate support ///	

Layers 1 and 4 also contained the dye mordant indicated in the previous examples.

Variations

- Example 14 contains Layers 1 and 2 only
 Example 15 contains 100 mg. of Lippmann-type emulsion/ft.² in Layer 3
 Example 16 contains 50 mg. of Lippmann-type emulsion/ft.² in Layer 3
 Example 17 contains 48 mg. of the fogged internal image emulsion and 303 mg. of gelatin/ft.² in Layer 1, and 130 mg. of the green-sensitized emulsion and 296 mg. of gelatin/ft.² in Layer 2
 Example 18 is like Example 17 and also contains 50 mg. of Lippmann emulsion/ft.² in Layer 3
 Example 19 is like Example 17 and also contains 100 mg. of Lippmann emulsion/ft.² in Layer 3
 Example 20 contains Layers 4 and 5 only

Four samples each of the Example 17 and Example 19 multilayer elements are exposed through a graduated density test object with blue light (Wratten filter No. 98) and then with green light (Wratten filter No. 99) and processed at 75° F. in the following sequence:

Development ^a	min.	6
Wash	sec.	30
F-5 Fix	min.	3
Wash	min.	3
Dye Bleach ^b	min. (resp.)	4, 8, 10, 15
Wash	min.	1
Cupric Bleach ^c	min.	8
F-5 Fix	min.	2
Wash	min.	5
Drying.		

^a Kodak D-72 type developer plus 0.1 g./liter 5-methylbenzotriazole (antifoggant).

^b See Example 13.

^c CuSO₄ (100 g.), 37% HCl (15 ml.) and water to 1 liter.

The D/log E curves of both the magenta dye image in Layer 1 and the yellow dye image in Layer 4 showed satisfactory bleach characteristics.

The identity of the yellow, magenta and cyan dyes used in the examples above is as follows: The yellow dye is Solantine Yellow 5435; the magenta dye is Solantine Pink 4BL, these being products of Allied Chemical Corp.; and the cyan dye is 8-acetamido-2[4-(8-amino-1-hydroxy-3,6-disulfo-2-naphthoazo)-2,5-methoxyphenylazo] - 1 - naphthol-3,6-disulfonic acid tetrasodium salt.

As the examples show, the silver-dye-bleach process comprises the following steps: (1) development of exposed silver halide under alkaline conditions; (2) oxidation of a metallic silver image in an acid medium by an organic oxidizing agent that functions as an electron carrier; (3) diffusion of the reduced form of the electron carrier from the silver surface through the gel matrix, and (4) irreversible reduction of the bleachable dye, normally an azo dye, to a colorless form with the accompanying oxidation of the electron carrier which can return to the silver surface for further reaction and which for this reason is often called a "catalyst."

As I have indicated, the development of the exposed silver halide is conventional black and white development in alkaline solutions of developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones or phenylenediamines. Particularly useful for development of silver iodide emulsions, which can be employed as the unfogged silver iodohalide emulsions in accordance with the invention, are the pyrogallol and related developers disclosed by James et al., *Phot. Sci. Eng.* 5, No. 1, 21-29 (1961). The developer solution may also contain auxiliary developing agents, such as 3-pyrazolidone compounds, e.g., 1-phenyl-3-pyrazolidone, as well as iodide compounds and/or silver halide solvents, as previously mentioned. It is also within the scope of the invention to incorporate developer compounds or developer precursors in a layer or layers of the photographic element. These are activated in conventional manner, for example, by treatment with an alkaline solution.

The silver-dye-bleach catalysts which oxidize the metallic silver image and serve as an electron carrier for reducing the bleachable dye can be selected from a wide range of known compounds of this type. These include various quinoxalines and phenazines disclosed, for example, in Gaspar U.S. Pat. 2,270,118. Examples of useful catalysts are listed below:

Phenazine; 2-hydroxy-3-aminophenazine; 2-anthraquinone sulfonic acid (Na salt); 2-methyl-3-(p-nitrophenyl) quinoxaline; 2-methyl pyrazine; 2-carbamyl pyrazine; 2,3,5,6-tetramethyl pyrazine; quinoxaline; 2-methyl quinoxaline; 6-chloro quinoxaline; 6-nitro quinoxaline; 6-methyl quinoxaline; 6-methoxy quinoxaline; 6,7-dimethyl quinoxaline; 2,3-bis(2-methyl-6-pyridyl)-6,7-dimethyl quinoxaline; 6,7-dimethyl-2,3-diphenyl quinoxaline; 6,7-dimeth-

yl-2,3-bis(2-pyridyl) quinoxaline; 2,3-diphenyl-6-nitro quinoxaline; 2,3,6,7-tetramethyl quinoxaline; 2,3-dimethyl quinoxaline; 2,3-diphenyl quinoxaline; 4-hydroxypteridine; 6,7-dimethyl-4-hydroxy-2-mercaptopteridine; 2,3(1,8-naphthyl) quinoxaline; 2-carboethoxy-3-methoxy quinoxaline.

Other useful catalysts are disclosed in the following U.S. Pats. 2,183,395; 2,669,517; 2,627,461; 2,578,710; 2,541,884; 2,410,025; 2,348,894; 2,341,034 and 2,270,118.

As indicated above, these compounds oxidize the metallic silver to silver ion, and in so doing, are reduced. The reduced catalyst then cross-oxidizes with the image dye. This cross-oxidation bleaches the image dye and oxidizes the catalyst back to its original state.

Compounds which are useful in oxidizing metallic silver to silver ion and which do not interact in their reduced form with the bleachable dyes can also be employed with the described catalyst. They are known as silver bleaching agents and include o- and m-nitrobenzene sulfonic acids and other typical silver bleaching agents as disclosed, for example, in British Pat. 533,190.

The photographic elements of this invention are not limited to the use of the particular dyes of the illustrative examples. In general any dyes and mordants suitable for conventional silver-dye-bleach materials can be used, including those disclosed, for example, in U.S. 3,414,411 and U.S. 3,498,787 and their cited references, and the neutral dye mixtures of British Pat. 999,996.

When used in a system with in-camera processing, the developer is placed in the usual pod with an alkaline activator, for example, as disclosed by Michel et al., U.S. Pat. 3,414,411. The acid, the bleach components, and the fixing agent are incorporated in the paper sheet that is normally used as the receiving layer in the solvent-transfer process. If necessary, a timing layer can be coated on top of this paper sheet to prevent premature release of the bleach and fix components. The contents of the pod are distributed over the surface of the exposed film in the usual way; then after a suitable time the contents of the paper sheet are released, forming a stable, positive dye image. This image may be viewed through the support, if the paper layer is laminated permanently to the top of the film.

The surface sensitive emulsions of the photographic elements of the invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. 1,623,499; Waller et al. U.S. Pat. 2,399,083; McVeigh U.S. Pat. 3,297,447; and Dunn U.S. Pat. 3,297,446.

Both types of emulsions in the photographic elements of the invention may contain speed-increasing compounds such as polyalkylene glycols, cationic surfact active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437; Dann et al. U.S. Pat. 3,046,134; Carroll et al. U.S. Pat. 2,944,900; and Goffe U.S. Pat. 3,294,540.

The surface sensitive silver halide emulsions can be protected against the production of fog and both types of emulsions can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. 2,131,038 and Allen et al. U.S. Pat. 2,694,716; the azaindenes described in Piper U.S. Pat. 2,886,437 and Heimbach et al. U.S. Pat. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. 3,236,652; the oximes described in Carroll et al. British Pat. 623,448; nitron; nitroindazoles; the mercaptotetrazaoles described in Kendall et al. U.S. Pat. 2,403,927; and Kennard et al. U.S. Pat. 3,266,897; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405; the thiuronium salts described in Herz et al.

U.S. Pat. 3,220,839; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. 2,566,263 and Yutzy et al. U.S. Pat. 2,597,915.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonates esters sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch and oxyguarum and the like.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. 3,142,568, issued July 28, 1964; White U.S. Pat. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911, issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing, and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic elements used with this invention may contain antistatic or conducting layers. Such layers may comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. 2,861,056 and Sterman et al. U.S. Pat. 3,206,312 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. 3,428,451.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetate) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and relates films of resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

The photographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton et al. U.S. Pat. 2,960,404; fatty acids or esters such as those described in Robijns U.S. Pat. 2,588,765 and Duane U.S. Pat. 3,121,060; and silicone resins such as those described in Du Pont British Pat. 955,061.

The photographic layers employed in the practice of this invention may contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. 2,600,831; amphoteric

compounds such as those described in Ben-Ezra U.S. Pat. 3,133,816; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. 1,022,878.

5 The photographic elements employed in the practice of this invention may contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al. U.S. Pat. 2,992,101 and Lynn U.S. Pat. 2,701,245.

10 Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the surface sensitive silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. 1,154,781. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

20 Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748; and Taber et al. U.S. Pat. 3,384,486. Spectral sensitizers which can be used include the cyanines merocyanines, complex (tri or tetranuclear) merocyanines, comple (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols.

30 Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

40 The merocyanine dyes may contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoin, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei may be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes may be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. 2,933,390 and Jones et al. U.S. Pat. 2,937,089.

55 The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. 3,253,921; Gaspar U.S. Pat. 2,274,782; Silberstein et al. U.S. Pat. 2,527,583 and VanCampen U.S. Pat. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Jones et al. U.S. Pat. 3,282,699.

The sensitizing dyes and other addenda used in the practice of this invention may be added from water solutions or suitable organic solvent solutions may be used.

65 The compounds can be added using various procedures including those described in Collins et al. U.S. Pat. 2,912,343; McCrossen et al. U.S. Pat. 3,342,605; Audran U.S. Pat. 2,996,287 and Johnson et al. U.S. Pat. 3,425,835.

The photographic layers used in the practice of this invention may be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguni U.S. Pat. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. 2,761,791 and Wynn British Pat.

837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. 968,453 and LuValle et al. U.S. Pat. 3,219,451.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A silver-dye-bleach photographic element comprising a support, a silver halide emulsion layer comprising fogged internal latent images silver halide grains and, in an adjacent layer, an unfogged emulsion comprising surface latent image silver iodohalide grains, said fogged emulsion layer containing a dye which is bleachable in the presence of developed silver.

2. A photographic element according to claim 1 in which said fogged emulsion layer also contains a development fog inhibitor.

3. An element according to claim 2 in which said fogged emulsion layer comprises a silver chlorobromide-gelatin internal latent image emulsion positioned between the support and an adjacent unfogged emulsion layer which comprises a silver bromiodide-gelatin emulsion.

4. A photographic element comprising at least three pairs of fogged and unfogged emulsion layers which are coated sequentially over the support and comprise, in the direction from the support to the upper surface of the element, (1) a fogged emulsion layer comprising internal latent image silver halide grains and a cyan dye which is bleachable in the presence of developed silver, (2) an unfogged red-sensitized emulsion layer comprising surface latent image silver iodohalide grains, (3) a fogged emulsion layer comprising internal latent image silver halide grains and a magenta dye which is bleachable in the presence of developed silver, (4) an unfogged green-sensitized emulsion layer comprising surface latent image silver iodohalide grains, (5) a fogged emulsion layer comprising internal latent image silver halide grains and a yellow dye which is bleachable in the presence of developed silver, and (6) an unfogged blue-sensitive emulsion layer comprising surface latent image silver iodohalide grains.

5. A photographic element according to claim 4 in

which the fogged internal latent image emulsion layers contain a mercapto development antifoggant.

6. A photographic element according to claim 4 in which a barrier layer which inhibits the migration of iodide ion is positioned between each unfogged silver iodohalide emulsion layer and the overlying fogged emulsion layer.

7. A photographic element according to claim 5 in which said barrier layers comprise an insensitive fine grain silver halide emulsion layer.

8. A photographic element according to claim 7 in which each barrier layer contains a ballasted para-quinone diffusion-inhibiting agent and at least the barrier layer above the green-sensitized emulsion layer contains a blue-light filtering material.

9. A photographic element comprising a support which has coated on each of its surfaces a silver halide emulsion layer of fogged internal latent image silver halide grains containing a dye which is bleachable in the presence of developed silver and, coated over each of said layers, an unfogged surface latent image silver iodohalide emulsion layer.

10. A photographic element according to claim 9 in which the fogged internal latent image emulsion layer contains a mixture of dyes which yield a neutral image, such dyes being bleachable in the presence of developed silver.

References Cited

UNITED STATES PATENTS

2,996,382	8/1961	Luckey et al.	96—68
3,418,123	12/1968	Haugh	96—63
3,505,068	4/1970	Beckett	96—74

FOREIGN PATENTS

818,687	8/1959	Great Britain	96—68
1,027,146	4/1966	Great Britain	96—67
923,045	4/1963	Great Britain	96—74

J. TRAVIS BROWN, Primary Examiner

J. R. HIGHTOWER, Assistant Examiner

U.S. Cl. X.R.

96—95, 53, 20