

1

3,445,231

ANTI-HALATION LAYER FOR SILVER HALIDE LIGHT-SENSITIVE MATERIALS

Fumihiko Nishio, Daijiro Nishio, Syo Watarai, Yoshihide Hayakawa, Hirotetu Kato, and Hirozo Ueda, Kanagawa, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Kanagawa, Japan

No Drawing. Filed Mar. 18, 1966, Ser. No. 535,315

Claims priority, application Japan, Mar. 29, 1965,

40/17,941

Int. Cl. G03c 1/84

U.S. Cl. 96—84

16 Claims

ABSTRACT OF THE DISCLOSURE

Silver halide light-sensitive material comprising a support, at least one silver halide emulsion layer and an anti-halation layer, said anti-halation layer consisting of a hydrophilic colloid layer having incorporated therein a polymer containing more than 50 percent of 2-methyl-1-vinylimidazole and a dyestuff having an acid group.

This invention relates to a photographic silver halide light-sensitive material having a layer containing a dyestuff resistant to diffusion for preventing the formation of halation.

It is well known that in photographic light-sensitive materials, the sharpness of the image is increased by preventing the formation of halation at exposure. Various methods have been provided for preventing the formation of halation. For example, there has generally been employed a method in which a layer for absorbing the light effective for sensitization is placed between a light-sensitive layer and a support, a method in which a material for absorbing such light is incorporated in the support, and a method in which such an absorbing layer is formed on the surface of the support opposite to the light-sensitive layer. The above-mentioned first and second methods are most effective for the prevention of the formation of halation. However, there are difficulties in the first method in that the material for absorbing the effective light has been diffused from the intermediate layer into the light-sensitive layer. This reduces the sensitivity and gradation of the light-sensitive layer. Also, if the material has not been diffused out of the intermediate layer, it remains in the layer after developing fixing and water-washing have been completed. This results in darkening of the formed image. Further, the second method can be used for only a limited use since the absorbing material remains, in general, in the support after processing.

These difficulties accompanying the application of the first method or the second method may be overcome in accordance with the abovescribed third method, but the presence of a comparatively thick support layer between the light-sensitive layer and the anti-halation layer reduces the anti-halation effect of the layer itself.

Accordingly, it is most preferable that in the first method the absorbing material is not present in the light-sensitive layer by diffusion before exposure and the material will be removed from the intermediate layer by diffusion or decolorized by a chemical action at development after exposure. As an example of such improvements, the use of a colloidal silver particle has been proposed but while it is used effectively for color photographic materials, it cannot be effectively used for black and white photo-

2

graphic materials. Hence, in order that such means be used for black and white photographic materials, the use of dyestuffs instead of the use of colloidal silver is desirable.

Therefore, an object of this invention is to provide an anti-halation layer containing therein a dyestuff capable of absorbing light effective to sensitization, wherein the diffusion of the dyestuff into the light-sensitive layer before exposure is kept as small as possible, after the anti-halation layer is coated on the light-sensitive layer and the dyestuff is easily decolorized by the developing, fixing and water-washing treatments after exposure.

This object can be achieved by using as the anti-halation layer a layer of a hydrophilic colloid, such as gelatin, containing (1) a polymer composed of more than 50% of 2-methyl-1-vinylimidazole and (2) a dyestuff having an acid group. If the content of 2-methyl-1-vinylimidazole in the polymer is less than 50%, the polymer is ineffective for the present invention.

As the light-sensitive layer to which the anti-halation layer of this invention is utilized, a silver halide photographic emulsion layer can be used and particularly a photographic silver halide emulsion sensitized optically and having a high resolving power can be profitably used.

On practicing this invention, after applying an under coating to the surface of a film support composed of a high-molecular material, such as, triacetyl cellulose or polyethylene terephthalate to provide an adhesive power to a hydrophilic colloid layer such as a gelatin layer, the anti-halation layer of this invention is applied to thus treated film and on the anti-halation layer is applied a silver halide photographic emulsion layer and, if necessary, a protective layer. In this invention, further, a paper may be used as the support.

In order to facilitate the application of a photographic silver halide emulsion layer to the anti-halation of this invention, the anti-halation layer may contain various surface active agents, such as saponin, sodium alkylbenzene sulfonate, polyoxyethylene alkylphenyl ether and the like.

The gelatin used in this invention may be one prepared by lime-treating or acid-treating a raw material, such as oxhides, ox bones, and pig hides.

For increasing the strength of the film, a hardening agent, such as formaldehyde, mucochloric acid, chlorotriazine derivatives, and the like may be used and moreover, a hardening acid, such as resorcinol, resorcy aldehyde and the like may be used together with the hardening agent.

Further, a stabilizer for photographic emulsion, such as 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, etc., may be added in the anti-halation layer of this invention to increase the photographic properties of the emulsion layer.

Furthermore, a low-sensitive photographic silver halide emulsion may be dispersed in the anti-halation layer of this invention to improve the gradation of the light-sensitive material.

Still further, the anti-halation layer in this invention may be used as the intermediate layers for each light-sensitive layer of a multi-layer color photographic material to prevent the formation of halation in the upper layers and at the same time to suppress undesirable optically sensitive areas in the lower layers.

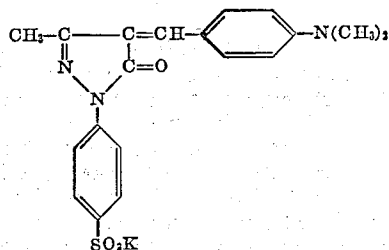
A suitable amount of dyestuff used in this invention is 1 to 20 g. per 100 g. of dried gelatin and that of the polymer is 2 to 40 g. per 100 g. of dried gelatin.

3

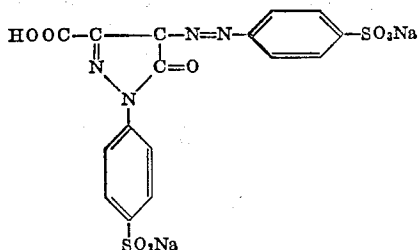
The following examples of the practical dyestuffs used in this invention, the examples for the synthesis of the polymers used in this invention and the examples of this invention will serve to understand this invention in detail, but it should be understood that the invention is not limited to the examples.

Typical examples of the dyestuffs used in this invention are as follows:

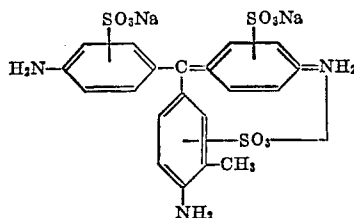
Dyestuff 1



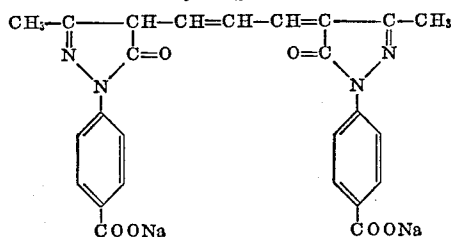
Dyestuff 2



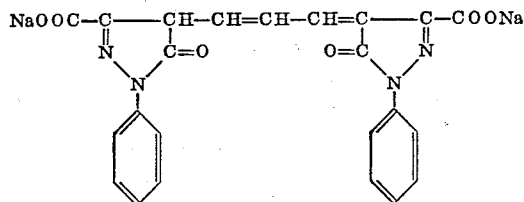
Dyestuff 3



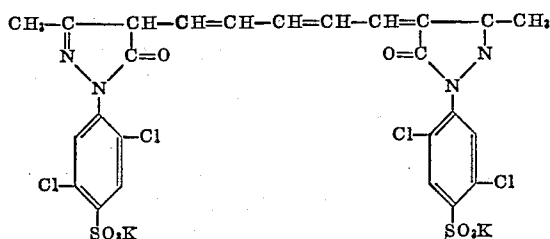
Dyestuff 4



Dyestuff 5

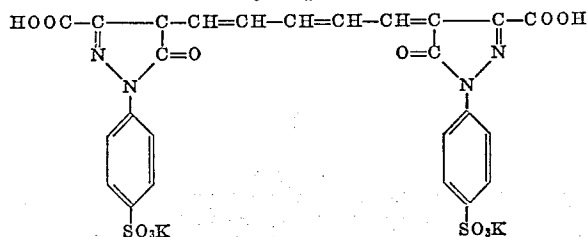


Dyestuff 6

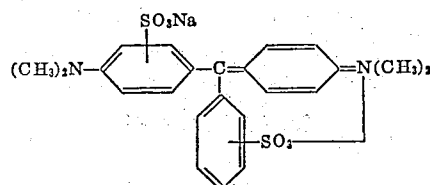


4

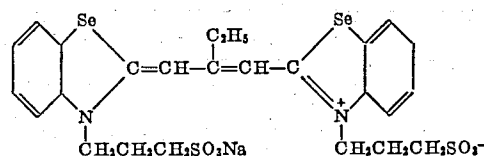
Dyestuff 7



Dyestuff 8



Dyestuff 9



Typical examples of the dyes used in this invention were shown above, but it should be understood that dyes of this invention shall not be limited to these compounds, but may be ones containing acid groups, such as a sulfonate group and carboxylate group, which are decolorized during processing.

The following are the practical examples for synthesizing the polymers used in this invention.

Synthesis 1.—In 500 ml. of methanol was dissolved 150 g. of 2-methyl-1-vinylimidazole, and after the addition of 0.3 g. of azobis-isobutyronitril, the mixture was stirred for 3 hours at 60° C. in a nitrogen stream. After the end of reaction, 500 ml. of acetone was added into the reaction product and the mixture was poured in an excessive amount of ether with stirring, whereby 110 g. of poly-2-methyl-1-vinylimidazole was precipitated.

Synthesis 2.—Into 700 ml. of water were dissolved 200 g. of 2-methyl-1-vinylimidazole and 1 g. of sodium bisulfate and then a solution of 1 g. of potassium persulfate in 100 ml. of water was added into the solution with stirring in a nitrogen stream. The mixture was stirred for 4 hours at 35° C., subjected to dialysis in a water stream for one night, and dried by freezing to provide 190 g. of poly-2-methyl-1-vinylimidazole.

Synthesis 3.—Into 70 ml. of water were dissolved 31 g. of 2-methyl-1-vinylimidazole, 9 g. of acrylamide and 0.2 g. of potassium persulfate, and after adding a solution of 0.2 g. of sodium bisulfate in 10 ml. of water, the mixture was stirred for 3 hours at 40° C. in a nitrogen stream. The solution was subjected to dialysis in a water stream for one night and then to drying by freezing to provide 35 g. of the copolymer.

Synthesis 4.—Into an aqueous solution of 35% isopropyl alcohol were dissolved 66.2 g. of 2-methyl-1-vinylimidazole and 33.8 g. of N-ethoxymethyl acrylamide to make the whole volume 500 ml. and after the addition of 2 ml. of 30% hydrogen peroxide solution and 0.5 g. of L-ascorbic acid, the mixture was stirred for 5 hours at 40° C. in a nitrogen stream. The solution was subjected to dialysis in a water stream for one night and dried by freezing to provide 85 g. of the copolymer.

Synthesis 5.—Into 150 ml. of water were dissolved 25.5 g. of 2-methyl-1-vinylimidazole, 14.5 g. of acryloylmorpholine, and 0.2 g. of potassium persulfate and, after the addition of a solution of 0.2 g. of sodium persulfate in 10 ml. of water, the mixture was stirred for 4 hours

5

at 40° C. in a nitrogen stream. The solution was subjected to dialysis for one night in a water stream and dried by freezing to give 27 g. of the copolymer.

Synthesis 6.—Into 150 ml. of water were dissolved 28 g. of 2-methyl-1-vinylimidazole, 12 g. of 1-vinylpyrrolidone and 0.2 g. of potassium persulfate and, after the addition of a solution of 0.2 g. of sodium bisulfate in 10 ml. of water, the mixture was stirred for 4 hours at 40° C. in a nitrogen stream. The solution was subjected to dialysis for one night and dried by freezing to provide 30 g. of the copolymer.

Synthesis 7.—Into 150 ml. of water were dissolved 29 g. of 2-methyl-1-vinylimidazole, 11 g. of N-methylol acrylamide, and 0.2 g. of ammonium persulfate and after the addition of a solution of 0.2 g. of sodium bisulfate in 10 ml. of water, the mixture was stirred for 2 hours at 40° C. in a nitrogen stream. The solution was subjected to dialysis for one night in a water stream and dried by freezing to provide 30 g. of the copolymer.

Example 1

Into 50 ml. of an aqueous solution containing 5 g. of gelatin, 0.1 g. of saponin, and 0.1 g. of mucochloric acid was added 8 ml. of a 5% aqueous solution of the polymer obtained in Synthesis 1 and then were added the 2% aqueous solutions of Dyestuffs 1, 4, and 6 in an amount of 10 ml. each. After adjusting the pH of the solution to 6.5 with the addition of sodium carbonate, the solution was added with water up to 100 ml. (Sample A.)

As a comparative sample, the solution without containing the polymer was prepared by the same procedure as above. (Sample B.)

Each of the above-prepared solutions was applied to a film base of triacetyl cellulose having a colorless under coating in a dried thickness of 2 microns. A fine silver bromo-chloride particle emulsion containing 40 mol percent of silver chloride optically sensitized into panchromatic state and gelatin in an amount of 120 g. per 1 mol of the silver halide was applied onto the layer in a dried thickness of 2 microns, and on thus formed layer was further applied a protective layer consisting of gelatin and a hardening agent in a dried thickness of 1 micron.

Further, for comparison, a sample consisting of a film base having thereon only an emulsion layer and a protective layer was prepared. (Sample C.)

When thus prepared films using Samples A and B were treated with a usually available developing solution and fixing solution and then washed with water, the dyestuffs were easily decolorized.

On the other hand, when the photographic sensitivities of the films were compared, that of the film using Sample B was reduced to about 50% of that of Sample C, while that of the film using Sample A was reduced to only 20% of that of Sample C. Further, it was confirmed that the sharpness of images in the films using Samples A and B were greatly improved as compared with that in Sample C. That is, by using Sample A, the sharpness could be increased with a smaller reduction in sensitivity.

It was further confirmed by microscopic observation that in the case of using Sample A the dyestuff was scarcely diffused into the emulsion layer but in the case of using Sample B the dyestuff was markedly diffused into the emulsion layer.

Example 2

The same procedure was repeated using 11 ml. of a 5% aqueous solution of the polymer prepared in Synthesis 3 instead of the polymer in Example 1 and using 10 ml. each of the 2% aqueous solutions of Dyestuffs 2, 4, and 8. Almost in the same results as in Example 1 were obtained.

Example 3

The same procedure as in Example 1 was repeated using 15 ml. of a 5% aqueous solution of the polymer

6

prepared in Synthesis 6 instead of using the polymer in Example 1 and using 10 ml., 8 ml., and 10 ml. each of the 2% aqueous solutions of Dyestuffs 2, 5, and 8 respectively. Almost the same results as in Example 1 were obtained.

Example 4

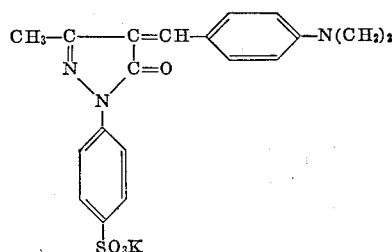
A coating solution was prepared as in Example 1 using 3 ml. of an 0.1% aqueous solution of Dyestuff 9 instead of the aqueous solutions of Dyestuffs 1, 4, and 6 in Example 1 and the coating solution was applied to a red-sensitive layer of a multi-layer type color photographic element in a dried thickness of 1 micron. On the thus formed layer were applied a green-sensitive layer, a yellow colloidal silver layer, blue-sensitive layer and then a protective layer.

As comparative sample, a Sample A' and a Sample B' were prepared respectively by applying a coating solution Dyestuff 9 but containing no polymer on the red-sensitive layer of the color photographic element and by applying a coating solution containing neither Dyestuff 9 nor polymer on the red-sensitive layer. When these samples and the above prepared light-sensitive material of this invention were treated by a standard color-reversal treatment, the color residue of the dyestuff was not observed in each sample. On the other hand, it was found that the undesirable green-sensitivity of the red-sensitive layer of the light-sensitive material of this invention was reduced to 50% as compared with that of Sample B while the green-sensitivity of the red-sensitive layer of the light-sensitive material was reduced to only 20%. Further, it was found that the red-sensitive layer and the green-sensitive layer of Sample A' were reduced into 50% in green-sensitivity as compared with Sample B'.

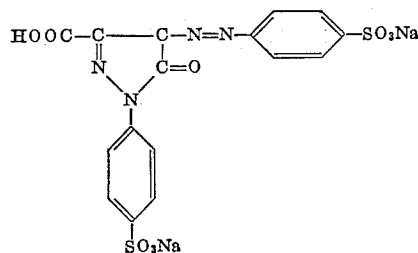
What we claim is:

1. A silver halide light-sensitive material comprising a support, at least one silver halide emulsion layer and an anti-halation layer, said anti-halation layer consisting of a hydrophilic colloid layer having incorporated therein (1) a polymer containing more than 50% of 2-methyl-1-vinylimidazole polymerized therein and (2) a dyestuff having a salt of an acid group.

2. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



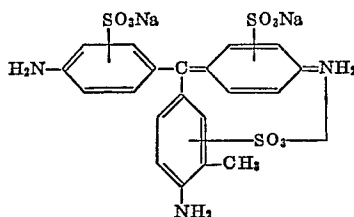
3. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



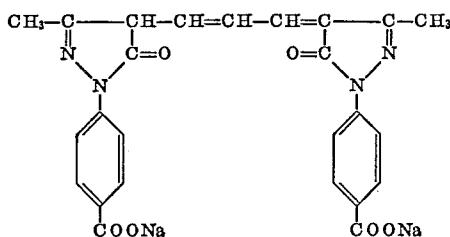
4. The silver halide light-sensitive material as claimed

7

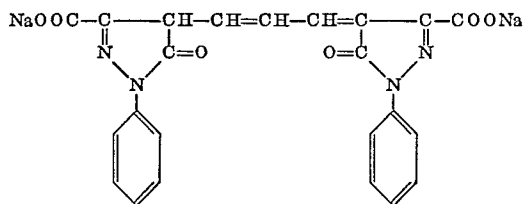
in claim 1 wherein said dyestuff is one having the formula:



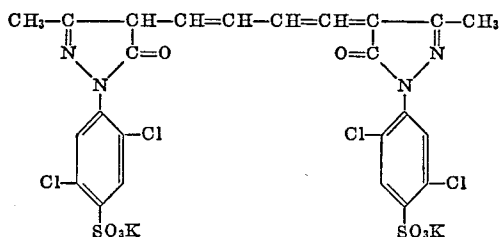
5. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



6. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



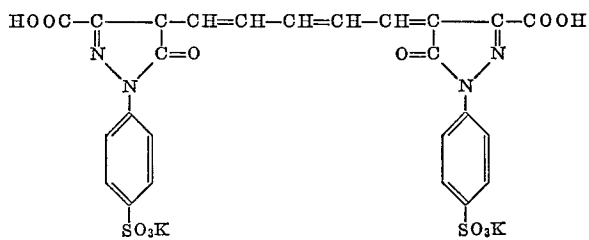
7. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



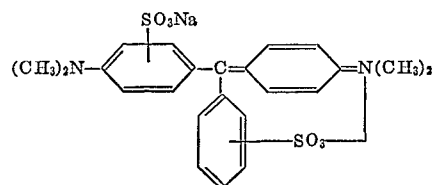
8. The silver halide light-sensitive material as claimed

8

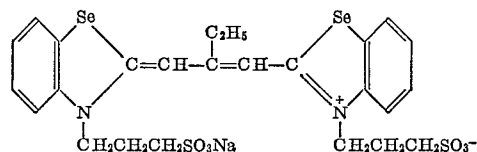
in claim 1 wherein said dyestuff is one having the formula:



9. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



10. The silver halide light-sensitive material as claimed in claim 1 wherein said dyestuff is one having the formula:



11. The silver halide light-sensitive material as claimed in claim 1 wherein the amount of said polymer is 2 to 40 g. per 100 g. of dried gelatin in said anti-halation layer and the amount of said dyestuff is 1 to 20 g. per 100 g. of the dyestuff.

12. The silver halide light-sensitive material as claimed in claim 1 wherein said anti-halation layer is present between the silver halide light-sensitive emulsion layer and an under coating for said support.

13. The silver halide light-sensitive material as claimed in claim 1 wherein said light-sensitive material is a multi-layer type color photographic material and said anti-halation layer is an intermediate layer for each light-sensitive layer.

14. The silver halide light-sensitive material as claimed in claim 1 wherein said anti-halation layer further contains a hardening agent.

15. The silver halide light-sensitive material as claimed in claim 1 wherein said anti-halation layer further contains a stabilizer.

16. The silver halide light-sensitive material as claimed in claim 1 wherein said anti-halation layer further contains a low-sensitive silver halide particle.

References Cited

UNITED STATES PATENTS

2,182,794 12/1939 Dawson.

NORMAN G. TORCHIN, *Primary Examiner*.

J. R. HIGHTOWER, *Assistant Examiner*.