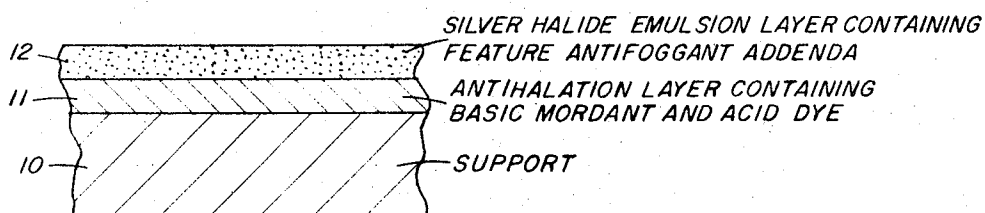


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C. M. KRETCHMAN ET AL
PHOTOGRAPHIC ELEMENTS HAVING SILVER HALIDE EMULSION
LAYERS COATED ADJACENT TO MORDANT-DYE LAYERS
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3,449,122



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1

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PHOTOGRAPHIC ELEMENTS HAVING SILVER HALIDE EMULSION LAYERS COATED ADJACENT TO MORDANT-DYE LAYERS

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17 Claims 10

ABSTRACT OF THE DISCLOSURE

Improved photographic elements comprising a hydrophilic layer containing a dye and a mordant adjacent to a silver halide emulsion layer comprising certain cyclic ketone antifoggants are disclosed.

The present application relates to photographic elements having a silver halide emulsion layer coated adjacent to a mordant-dye layer, and more particularly, to the stabilization of such a silver halide emulsion layer against fog formation.

Photographic elements containing a layer wherein an acid dye is mordanted therein with a basic mordant and adjacent silver halide emulsion layer are described in French Patent 1,359,682, issued Mar. 24, 1964, and Belgian Patent 627,308, granted Feb. 15, 1963. However, fog formation in the silver halide emulsion of such elements is particularly difficult to inhibit or control, particularly with negative speed silver bromoiodide emulsions.

The term "fog" as used herein refers to chemical fog. Such fog manifests itself as a detectable amount of silver that is formed during development in areas where no exposure was made. Such fog is to be distinguished from the effects of accidental exposure of a silver halide emulsion to radiation.

It is an object of this invention to provide a novel photographic element containing a mordant-dye layer adjacent to a silver halide emulsion layer inhibited against fog formation.

It is another object of this invention to provide a novel photographic element wherein a mordanted dye layer is coated adjacent to a silver halide emulsion layer, and when such a photographic element is exposed and chemically developed, an image having high D_{max} results.

These and other objects of the invention are accomplished with photographic elements comprising a support having coated thereon a photographic silver halide emulsion layer adjacent to a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant, the silver halide emulsion layer containing a cyclic ketone antifoggant.

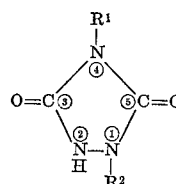
The cyclic ketones utilized in the silver halide emulsion layers comprising the photographic emulsions of the invention typically are urazoles or anthraquinones containing at least one acid radical such as a sulfo ($-\text{SO}_3\text{H}$) or a carboxyl



radical, and including conventional salts thereof.

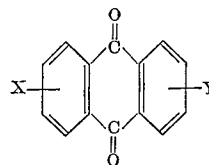
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Typical urazoles that can be used in the subject silver halide emulsions as antifoggants can be represented by the formula



wherein R^1 and R^2 can each be a hydrogen atom, an aryl radical such as naphthyl or phenyl, or an alkyl radical typically having 1 to 20 carbon atoms, and more generally, 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl, amyl, octyl, decyl, dodecyl, octadecyl, eicosyl, etc., and including substituted aryl and alkyl radicals. Illustrative suitable urazoles include: urazole, 4-phenylurazole, 4-(1-naphthyl)urazole, 4-ethylurazole, 1-phenylurazole, 1-butylurazole, 1-octylurazole, 1,4-diphenylurazole, 1,4-dibutylurazole, 1-ethyl-4-phenylurazole and the like.

Typical anthraquinones having acid groups that can be used in the subject silver halide emulsions as antifoggants can be represented by the formula



wherein X and Y represent a hydrogen atom or at least one acid group such as sulfo or carboxy radicals, at least one of X and Y being an acid group. Illustrative suitable anthraquinones include: anthraquinone-1-sulfonic acid, anthraquinone-2-sulfonic acid, anthraquinone-1,8-disulfonic acid, anthraquinone-1-carboxylic acid, anthraquinone-2-carboxylic acid, anthraquinone-1,8-dicarboxylic acid and the like, and which are generally added to the emulsion as salts thereof such as the alkali metal (e.g., sodium and potassium) and ammonium salts.

The stabilizing or antifoggant amount of the subject cyclic ketone antifoggants can be varied in accordance with usual practice. The urazole antifoggants are more usually used at a concentration of about .1 to 10 grams per mole of silver halide in the emulsion being stabilized, and the anthraquinones are more usually used at a concentration of about 1 to 100 mg. per mole of silver halide in the emulsion being stabilized. Exposure of the subject photographic elements in conventional photographic testing apparatus, such as an intensity scale sensitometer, will reveal the most advantageous concentrations for the present antifoggants in a particular silver halide emulsion. Such techniques are well understood by those skilled in the present art.

The cyclic ketone antifoggants used in the silver halide emulsion layers of the photographic elements of the invention can be added to the emulsions using any of the well-known techniques in emulsion making. For example, they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the tech-

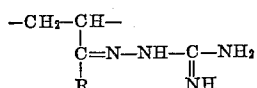
nique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al., U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al., U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice and generally solvents or diluents which are miscible with water are to be preferred.

In addition to the subject antifoggant addenda, the silver halide emulsion layers used in the invention can contain the usual well-known emulsion addenda such as spectral sensitizers, speed-increasing materials (e.g., polyalkylene glycols, cationic compounds, thioethers, etc.), coating aids, gelatin hardeners, plasticizers and the like.

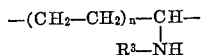
Conventional silver halides can be used as the light-sensitive material in the silver halide emulsion layers comprising the photographic elements of the invention. Typical suitable halides include silver bromide, silver chloride, silver iodide, silver bromiodide, silver chlorobromide and silver chlorobromiodide. The cyclic ketone antifoggants described above are particularly effective in negative speed silver bromiodide emulsion layers coated adjacent to mordant-dye layers.

A wide variety of nondiffusible basic mordants and acid dyes can be utilized in the mordant-dye layer positioned adjacent to a silver halide emulsion layer containing the above-described cyclic ketone antifoggants. Typical of such mordant-dye layers are disclosed in copending Jones and Milton application, U.S. Ser. No. 167,666, filed Jan. 22, 1962, now Patent No. 3,282,699, which corresponds to French Patent 1,359,682, issued Mar. 24, 1964, and Belgian Patent 627,308, granted Feb. 15, 1963. Other references disclosing useful nondiffusible basic mordants and acid dyes include the following U.S. patents: 2,274,782, issued Mar. 3, 1942; 2,484,430, issued Oct. 11, 1949; 2,606,834, issued Aug. 12, 1952; 2,675,316, issued Apr. 13, 1954; 2,753,263, issued July 3, 1956; 2,768,078, issued Oct. 23, 1956; 2,882,156, issued Apr. 14, 1959; and 3,016,306, issued Jan. 9, 1962.

The nondiffusible basic mordants that are utilized can be polymeric materials containing recurring basic units or ballasted monomeric basic compounds. A particularly useful class of mordants are vinyl polymers having a recurring structure unit with the structure



wherein R is an alkyl radical having 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl and iso-butyl. Examples of other useful basic mordants include linear polymers of monoethylenically unsaturated polymerizable compounds having periodically occurring dialkylamino groups attached thereto such as polydiethylamino ethyl methacrylate, polymeric polyamides having a recurring structural unit with the structure

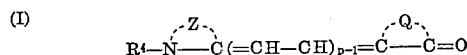


wherein n is an integer of 3 to 40 and R^3 is a hydrogen atom or an alkyl radical having 1 to 12 carbon atoms, N -substituted polyvinyl amines prepared by reacting alkyl or aryl polyvinyl sulfonates and aminopyridines or alkyl group substituted aminopyridines, triphenyl guanidine acetate, and the like basic mordants well known to those knowledgeable in the art.

Also, a wide variety of acid dyes can be utilized in the mordant-dye layer of the photographic elements of the invention. Such dyes are well known in the art. Particularly useful acid dyes are merocyanine dyes having substituted on the nucleus at one end of the dye molecule an acidic radical such as a sulfo radical, a sulfoalkyl radical, a sulfophenyl radical, a carboxy radical or a carboxy-alkyl radical, and similarly substituted on the nucleus at

the other end of the dye molecule another of such acid radicals. Benzoxazole pyrazolone merocyanine acid dyes are particularly useful.

Included among the dyes that are advantageously used according to our invention are those having the formula:

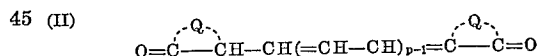


wherein R^4 represents an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, etc., or a carboxyalkyl group, such as carboxymethyl, carboxyethyl, carboxypropyl, etc., or a sulfoalkyl group, such as sulfoethyl, sulfopropyl, sulfobutyl, etc.; Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzoxazole series (including benzoxazole and benzoxazole substituted with substitutions such as methyl, ethyl, phenyl, methoxy, ethoxy, chlorine, bromine, etc.) or a nucleus of the benzoxazole series which has a sulfo substituent on the benzene ring as well as one or more of the above-mentioned simple substituents, such that when R^4 represents an alkyl group, Z represents the sulfo-substituted benzoxazole nucleus and when R^4 represents a carboxyalkyl group or a sulfoalkyl group, Z represents the nonmetallic atoms necessary to complete a benzoxazole nucleus; Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the sulfophenyl pyrazolinone series and p is an integer from 1 to 3.

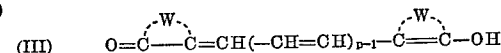
Typical representative dyes of Formula I include:

- 30 4-[(3-ethyl-2-(3H)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one, monosulfonated,
- 4-[4-(3-ethyl-2-(3H)-benzoxazolylidene)-2-butenylidene]3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one, monosulfonated,
- 35 4-[(3-β-carboxyethyl-2-(3H)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one,
- 40 4-[4-(3-β-ethyl-2-(3H)-benzoxazolylidene)-2-butenylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one.

Dyes which are used to advantage in our mordant-dye layers alone or in combination with dyes of Formula I include the oxonal dyes of formula:



wherein Q and p are as defined previously for Formula I, and the oxonol dyes of formula:



wherein W represents the nonmetallic atoms necessary to complete a 1-carboxyalkyl-3-hydrocarbon substituted hexahydro-2,4,6-trioxo-5-pyrimidine nucleus and p is as defined previously.

Typical examples of dyes having Formula II include dyes such as bis[1-(p-sulfophenyl)-3-methyl-2-pyrazolin-5-one(4)]-methinonol, bis[1-(p-sulfophenyl)-3-methyl-2-pyrazolin-5-one(4)]-trimethinonol, bis[1-(p-sulfophenyl)-3-methyl-2-pyrazolin-5-one(4)]-pentamethinonol, etc.

Typical examples of dyes having Formula III include dyes such as bis(1-butyl-3-carboxymethyl hexahydro-2,4,6-trioxo-5-pyrimidine)-trimethinonol, bis(1-butyl-3-carboxymethyl hexahydro-2,4,6-trioxo-5-pyrimidine)-pentamethinonol.

In preparing the silver halide emulsion layers or the mordant-dye layers used in the photographic elements of the invention, a wide variety of hydrophilic dispersing agents can be utilized. Gelatin or other colloids such as albumin, a cellulose derivative, or a synthetic resin, for example, a polyvinyl compound or polyacrylamide can be utilized. Likewise, mixtures of such colloids can be used. We prefer to use gelatin, however.

Typical supports that can be utilized for the photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials as well as glass, paper, polyolefin-coated paper, such as polyethylene- or polypropylene-coated paper, metals, wood and the like.

The photographic elements of the invention can take several forms with respect to the disposition of the mordant-dye layer and its adjacent silver halide emulsion layer containing the above-described cyclic ketone antifoggants. For example, the mordant-dye layer can be an antihalation layer coated adjacent to a photographic support, and a silver halide emulsion layer containing a cyclic ketone antifoggant coated directly over the mordant-dye layer. Such a disposition of layers can be used for either black-and-white or color photography. In another embodiment of the invention, the mordant-dye layer can be utilized as a filter layer, such as one containing a yellow dye to be used between an overcoated blue record layer of silver halide and an undercoated green or red record layer of silver halide in a multicolor photographic element in lieu of the more usually utilized yellow Carey Lea silver layer. The silver halide emulsion layers adjacent to such filter layers contain the cyclic ketone antifoggants described above. Similarly, the subject mordant-dye layer can be disposed to serve as a filter for other than a yellow Carey Lea silver filter layer in typical three-color photographic elements such as a magenta filter, for example, between an overcoated green record silver halide emulsion layer and an undercoated red record silver halide emulsion layer. Likewise, the subject mordant-dye layer could contain an ultraviolet absorbing dye and coated over a silver halide emulsion layer containing the above-described cyclic ketones to serve as an ultraviolet taking or exposure filter for the photographic element.

The subject photographic elements can thus be utilized in black-and-white photography or in color photography. In color photographic uses the silver halide emulsion layers can contain color-forming couplers or the emulsion layers can be developed by solutions containing couplers or other color-generating materials. Likewise, the subject photographic elements can be utilized in dye developer diffusion transfer processes when dye developers are incorporated contiguous to the silver halide, dye-bleach processes and related color processes.

The invention is illustrated by the figure of the drawing which sets out a typical embodiment of the invention. On support 10 is coated antihalation layer 11 which comprises an acid dye mordanted in the layer with a basic mordant. Over antihalation layer 11 is coated silver halide emulsion layer 12 which can contain one or more of the feature cyclic ketone antifoggant addenda described above.

The invention is further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

A photographic element of the type illustrated by the figure in the drawing is prepared. This photographic element in general comprises a cellulose acetate film support having coated thereon an antihalation layer comprising gelatin, a mordant, and a combination of acid dyes. The coating composition for the antihalation layer is an aqueous solution containing 4.54 grams gelatin, 1.34 grams poly(α -methyl alkyl-N-guanidylketimine), 0.27 gram saponin, 0.1165 gram 4-[(3-ethyl-2-(3H)-benzoxazolide)-ethylidene] - 3 - methyl - 1 - (p-sulfophenyl)-2-pyrazolin-5-one monosulfate, 0.0495 gram bis(1-butyl-3-carboxymethyl hexahydro-2,4,6-trioxo - 5 - pyrimidine)-trimethinoxonol, 0.1360 gram 4-[4-(3-ethyl - 2 - (3H)-benzoxazolylidene) - 2 - butenylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin - 5 - one monosulfonate, 0.0827 gram bis(1-butyl - 3 - carboxymethyl hexahydro-2,4,6-

trioxo-5-pyrimidine)pentamethinoxonol, and 0.0518 gram of bis[1-(p-sulfophenyl) - 3 - methyl-2-pyrazolin-5-one-(4)]-pentamethinoxonol in a total weight of 135.5 grams at a pH of 6.4. Over the antihalation layer is coated a coarse-grain sulfur-gold sensitized silver bromiodide galatin emulsion which is panchromatically sensitized with a cyanine dye. The silver halide emulsion is coated at a coverage of 450 mg. of silver per square foot. Similar coatings are prepared wherein various antifoggant addenda as described in the table are added to the silver halide emulsion prior to coating. A sample of each coating is incubated for seven days at 120° F. and 50% relative humidity. A freshly-prepared sample and an incubated sample for each of the coatings is exposed on an intensity scale sensitometer and reversal processed using the procedure described by C. E. Ives et al., "Processing Methods for Use with Two New Black-and-White Reversal Films," *SMPTE Journal*, vol. 66, No. 1, pages 1-11, January 1957. The following results are obtained. The amount of antifoggant addenda utilized is indicated in the table as milligrams or grams per mole of silver halide in the emulsion layer.

TABLE

Coating No.	Antifoggant addenda	Fresh tests		Incubation tests	
		D_{max}	Fog	D_{max}	Fog (1st dev.)
(1)-----	Control.....	2.30	.16	1.93	.25
(2)-----	Coating "(1)" +45 mg. sodium anthraquinone-1-sulfonate.	2.57	.11	2.29	.17
(3)-----	Coating "(1)" +1.75 g. 4-phenyl urazole.	2.57	.14	2.33	.15

Similar coatings containing other types of well-known antifoggants in place of the cyclic ketones set out in the table did not control the fog satisfactorily. For example, inorganic salts of the type described in U.S. Patent 2,839,405 issued June 17, 1958 (e.g., cadmium chloride), gold salts of the type described in U.S. Patent 2,597,915 issued May 27, 1952 (e.g., gold sulfide) and tetrazaindenes (e.g., 4-hydroxy-6-methyl-3,3,3a,7-tetrazaindene) when used as antifoggants for silver halide emulsion layers adjacent to layers containing acid dyes and basic mordants as described above resulted in processed photographic elements having fogs after incubation at least .10 to .25 greater than the coatings containing the cyclic ketones of the table. Also, when reversal processed as described above, the coatings containing the conventional antifoggants had D_{max} 's .30 to .50 less than the coatings containing the cyclic ketone antifoggants, after incubation.

EXAMPLE 2

A photographic element of the type described in Example 1 and illustrated by the drawing is prepared and results similar to those demonstrated by the data set out in the above table. Coatings 3 and 4, respectively, are obtained on incubation when 45 mg. per mole of silver halide of sodium anthraquinone-2-carboxylate or sodium anthraquinone-1,8-disulfonate is substituted for the sodium anthraquinone-1-sulfonate, and when two grams per mole of silver halide of 4-ethyl urazole is substituted for the 4-phenyl urazole.

The invention has been described in considerable 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 as described hereinabove and as defined in the appended claims.

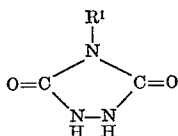
We claim:

1. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using a 4-alkyl radical or 4-aryl radical substituted urazole or anthraquinone containing

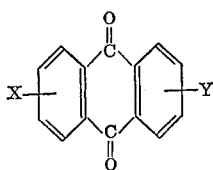
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at least one acid radical as an antifoggant in said silver halide emulsion layer.

2. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having a formula selected from the group consisting of



and



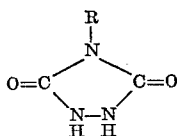
wherein R¹ is an aryl radical or an alkyl radical; and X and Y are each selected from the group consisting of a hydrogen atom, at least one carboxyl radical and at least one sulfo radical, except that at least one of X and Y is selected from the group consisting of a carboxy radical and a sulfo radical.

3. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a 4-alkyl radical or 4-aryl radical substituted urazole.

4. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of an anthraquinone containing at least one sulfo radical.

5. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of an anthraquinone containing at least one carboxyl radical.

6. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having the formula

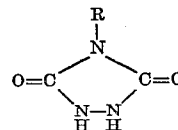


wherein F is a phenyl radical.

7. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improve-

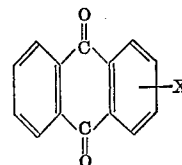
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ment which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having the formula



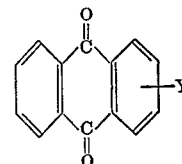
wherein R is an alkyl radical.

8. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having the formula



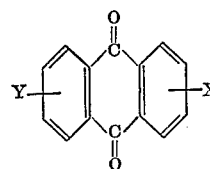
wherein X is a sulfo radical.

9. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having the formula



wherein Y is a carboxyl radical.

10. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer an antifoggant amount of a cyclic ketone having the formula



wherein X and Y are each sulfo radicals.

11. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer about .1 to 10 grams of 4-phenylurazole per mole of silver halide.

12. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer about 1 to 100 mg. of anthraquinone-1-sulfonic acid per mole of silver halide.

13. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide

emulsion layer about .1 to 10 grams of 4-ethylurazole per mole of silver halide.

14. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer about 1 to 100 mg. of anthraquinone-2-carboxylic acid per mole of silver halide.

15. In a photographic element comprising a hydrophilic layer containing a bleachable acid dye mordanted therein with a nondiffusible basic mordant positioned adjacent to a hydrophilic silver halide emulsion layer, the improvement which comprises using in said silver halide emulsion layer about 1 to 100 mg. of anthraquinone-1,8-disulfonic acid per mole of silver halide.

16. In a photographic element comprising a gelatin carrier containing a bleachable merocyanine acid dye mordanted with a poly(α -methyl alkyl-N-guanidylketimine) positioned adjacent to a gelatin-silver bromiodide emulsion layer containing about .1 to 10 grams of 4-phenylurazole per mole of said silver bromiodide.

17. In a photographic element comprising a gelatin carrier containing a bleachable merocyanine acid dye mordanted with a poly(α -methyl alkyl-N-guanidylketimine) positioned adjacent to a gelatin-silver bromiodide emulsion layer containing about 1 to 100 mg. of anthraquinone-1-sulfonate per mole of said silver bromiodide added to the emulsion as the sodium salt.

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96—109