(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 531 014 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92307545.1**

(51) Int. Cl.[5]: **G03C 1/06**, G03C 1/46

(22) Date of filing: **18.08.92**

(30) Priority: **03.09.91 US 753911**

(43) Date of publication of application:
10.03.93 Bulletin 93/10

(84) Designated Contracting States:
DE FR GB IT

(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center, P.O. Box 33427
St. Paul, Minnesota 55133-3427(US)

(72) Inventor: **Willett, Brian C., c/o Minnesota Mining and**
Manufact. Co., 2501 Hudson Road, P.O. Box 33427
St. Paul, Minnesota 55133-3427(US)

(74) Representative: **Baillie, Iain Cameron et al**
c/o Ladas & Parry, Altheimer Eck 2
W-8000 München 2 (DE)

(54) Multi-wavelength sensitive black-and-white graphic arts film.

(57) A black-and-white silver halide photographic element comprises at least two different silver halide emulsions each of which is spectrally sensitized to different wavelengths of the electromagnetic spectrum.

EP 0 531 014 A2

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to black-and-white silver halide photographic elements, and in particular to high contrast photographic elements with emulsions containing hydrazides. The elements may be used with various laser scanners in graphic arts or for imagesetter applications.

2. Background of the Art

Hydrazines find a variety of uses in silver halide photography. They have been used in negative working surface latent image forming silver halide emulsions to increase speed and/or contrast. They have been used in direct positive internal latent image forming emulsions as nucleating agents.

Hydrazines may also be used for internal latent image direct positive emulsions such as those described in U.S. Pat. No. 3,227,552 and reviewed in Research Disclosure No. 235 (1983) item 23510.

The most efficient hydrazines employed in silver halide photographic systems employ a combination of substituents to balance activity and stability. The stability of hydrazines is increased by attaching directly to one of the nitrogen atoms a tertiary carbon atom, such as the carbon atom of an aromatic ring. The art has long recognized that the activity of these stabilized hydrazines can be advantageously modified by the direct attachment of an acyl group to the remaining nitrogen atom. Thus the most commonly employed hydrazines are arylhydrazides.

Silver halide emulsions and/or developers containing hydrazines are disclosed, for example, in U.S. Pat. Nos. 2,419,975, 2,563,785, 3,227,552, 3,386,831, 3,730,727, 4,030,925, 4,031,127, 4,080,207, 4,168,977, 4,224,401, 4,243,739, 4,245,037, 4,255,511, 4,266,013, 4,272,614, 4,276,364, 4,323,643, 4,478,928 and 4,560,638 and U.K. Patent Specifications Nos. 1560005, 1579956, 2034908A and 2066492B.

In particular U.S. Pat. No. 2,419,975 discloses that high-contrast negative images are obtained by the addition of hydrazine compounds. This patent describes that extremely high-contrast photographic characteristics, such as a gamma (Υ) of more than 10, can be obtained by adding a hydrazine compound to a silver chlorobromide emulsion and developing at a pH as high as 12.8. However, the strongly alkaline developer having a pH of nearly 13 is susceptible to air oxidation and is too unstable to be stored or used for long periods.

U.S. Pat. No. 4,168, 977 discloses the use of a hydrazine of the formula:

$R^1NHNHCHO$

in which R^1 represents an aryl group, in combination with silver chlorobromide or silver chlorobromoiodide emulsions. This combination is capable of functioning at a lower pH than the hydrazines of U.S. Pat. No. 2,419,975 and a pH of 11.5 is exemplified.

U.S. Pat. No. 4,224,401 discloses the use of a hydrazine of the formula:

$R^1NHNHCOR^2$

in which R^1 an aryl group and R^2 is a hydrogen atom, C_1 to C_3 alkyl or phenyl optionally substituted with substitutents which are preferably electron withdrawing, in combination with silver bromide or silver iodobromide emulsions. This combination is also functional at a pH lower than that disclosed in U.S. Pat. No. 2,419,975 and a pH of 11.5 is exemplified when R^2 is hydrogen.

U.S. Pat. No. 4,925,832 describes a novel class of hydrazines which provide high contrast and undergo a cyclization process during their photographic activity. These are a preferred class of hydrazines.

At the present time, there are a number of different laser imaging systems used commercially. The most common of these systems are Argon ion lasers (which emit at 488 nm), helium-neon lasers (which emit at 633 nm), infrared lasers (which emit between 700 and 1300 nm, and especially at about 780, 800, 810, 830, 850 and 880 nm), and laser diodes (which can be designed to emit in portions of the visible through the infrared).

It is generally necessary for a film to be optimally spectrally sensitive to a narrow range of wavelengths. Unless different imaging systems emitted at similar wavelengths, a single film cannot be used for multiple systems. Each film is therefore generally optimized for a single imaging system.

It has not been found to be possible to take standard silver halide emulsions, even emulsions generally optimized for use with lasers, and sensitize them to three different wavelength regions (e.g., 400 to 550 esp., 488 nm, 600 to 680, esp.,633 nm, and 750-900, especially 780 nm) to provide an element with high densities and high speeds for all three laser sources unless very high silver coating weights (e.g., greater than 8.0 g/m^2) were used. It is desirable to produce a multiwavelength sensitive rapid processing high contrast photographic silver halide element.

SUMMARY OF THE INVENTION

A multiwavelength sensitive high contrast hydrazide-containing photographic silver halide element may be produced with a substrate carrying at least three different silver halide emulsion layers on the same side of the support. Each emulsion layer contains a black-and-white emulsion which is spectrally sensitized to a portion of the electromagnetic spectrum different from that to which the other emulsion layers are spectrally sensitized. A contrast enhancing hydrazide compound is present in at least one of the emulsion layers. This element can be imaged at any of the wavelengths to which any of the at least three emulsion layers has been spectrally sensitized and still provide high densities, high speed and high contrast. This can be done at silver coating weights below 5.0 g/m.

DETAILED DESCRIPTION OF THE INVENTION

The present invention describes a high contrast black-and-white silver halide photographic element which can be exposed by at least three different wavelengths of radiation and provide high speed imaging, high density images, and high contrast for each of the three different wavelengths.

A number of different types of photographic elements may be made according to the teachings of the present invention. For example, one may provide a black-and-white silver halide photographic element comprising a substrate having at least two silver halide emulsion layers thereon, the total weight of silver on said substrate being less than 5.0 g/m^2, said at least two silver halide emulsions being spectrally sensitized to at least two different wavelengths of the electromagnetic spectrum which differ by at least 50 nm, and at least one of said silver halide emulsion layers containing a contrast enhancing hydrazine. Additionally one may provide a black-and-white silver halide photographic element comprising a substrate having at least three silver halide emulsion layers thereon, each of said at least three silver halide emulsion layers being spectrally sensitized to different wavelengths of the electromagnetic spectrum which differ from each other by at least 50 nm, and the total weight of silver on said substrate being less than 5.0 g/m^2, at least one of said silver halide emulsion layers containing a contrast enhancing hydrazide.

It is desirable in the first construction to have one of said at least two different wavelengths within the infrared region of the spectrum and the emulsions layer spectrally sensitized to the infrared is not the outermost silver halide emulsion layer from said support.

It is also desirable in the second construction for one of said different wavelengths to be within the infrared region of the spectrum and the silver halide emulsion spectrally sensitized to the infrared is not the outermost silver halide emulsion layer from said support.

The present invention also teaches us a process for making a black-and-white silver halide photographic element comprising at least two separate black-and-white silver halide emulsions, separately spectrally sensitizing each of said silver halide emulsions to different wavelengths of the electromagnetic spectrum which differ by at least 50 nm, and coating said emulsions onto a support layer to form said element, said element additionally containing a contrast enhancing hydrazide in reactive association with said silver halide emulsion layers.

The process is particularly effective when said spectrally sensitized emulsions are coated onto said support as separate layers, and at least three separate emulsions are separately spectrally sensitized to at least three different wavelengths of the electromagnetic spectrum, and when said at least three separate emulsions are coated onto said support as separate layers.

The process is particularly desirable when one of said layers is spectrally sensitized to the infrared and that layers sensitized to the infrared is not the outermost silver halide emulsion layer from said support.

The sensitizing dyes used in the present invention are added to the silver halide emulsion in amounts of 5×10^{-7} mole to 1×10^{-2} mole, and most preferably in the amounts of 1×10^{-6} to 1×10^{-3} mole per mole of silver.

The sensitizing dyes are used to spectrally sensitize each of the different emulsions to the desired wavelengths for laser imaging. Reasonable sensitizing ranges would include 400 to 550 nm, 400 to 450 nm, 470 to 500 nm (esp. 488 nm), 600 to 680 nm (esp. 633 nm and 670 nm), 700 to 1300 nm, and 750 to 900 nm, (esp. 780 nm, 800 nm, 810 nm, 830 nm, 850 nm and 880 nm).

These sensitizing dyes are usually dissolved in a suitable solvent such as methanol, ethanol, dimethyl formamide, cellusolve, acetone, water, pyridine, or a mixture thereof before adding them to the emulsion. Once added, the mixture is stirred well and the dye compounds are added, usually just prior to coating.

Any of the various types of photographic silver halide emulsions may be used in the practice of the present invention. Silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodobromide and mixtures thereof may be used for example. Any configuration of grains, cubic orthorhombic, hexagonal, epitaxial, lamellar, tabular or mixtures thereof may be used. These emulsions are prepared by any of the well-known procedures, e.g., single or double jet emulsions as described by Wietz et al., U.S. Pat. No. 2,222,264, Illingsworth, U.S. Pat. No. 3,320,069, McBride, U.S. Pat. No. 3,271,157 and U.S. Pat. Nos. 4,425,425 and 4,425,426.

The silver halide emulsions sensitized with the dyes of this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed e.g., by the procedures described in Hewitson et al., U.S. Pat. No. 2,618,556; Yutzy et al., U.S. Pat No. 2,614,928; Yackel, U.S. Pat. No. 2,565,418; Hart et al., U.S. Pat. No. 3,241,969; and Waller et al., U.S. Pat. No. 2,489,341.

Photographic emulsions in accordance with this invention can 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 chemical sensitization procedures are described in Shepard, U.S. Pat. No. 1,623,499; Waller, U.S. Pat. No. 2,399,083; McVeigh, U.S. Pat. No. 3,297,447; and Dunn, U.S. Pat. No. 3,297,446.

The sensitized silver halide emulsions of this invention can contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper, U.S. Pat. No. 2,886,437; Chechak, U.S. Pat. No. 3,046,134; Carroll et al., U.S. Pat. No. 2,944,900; and Goffe, U.S. Pat. No. 3,294,540.

Silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers which can be used alone or in combination, include the thiazolium salts described in Staud, U.S. Pat. No. 2,131,038 and Allen U.S. Pat. No. 2,694,716; the azaindenes described in Piper, U.S. Pat. No. 2,886,437 and Heimbach, U.S. Pat. No. 2,444,605; the mercury salts described in Allen, U.S. Pat. No. 2,728,663; the urazoles described in Anderson, U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard, U.S. Pat. No. 3,235,652; the oximes described in Carrol et al., British Patent 623,448; nitroindazoles; the polyvalent metal salts described in Jones, U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz, U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli, U.S. Pat. No. 2,566,263 and Damschroder, U.S. Pat. No. 2,597,915.

Silver halide emulsions in accordance with the invention can be dispersed in colloids that 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, sulfonate esters, sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compound, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum, etc.

Photographic emulsions described herein can contain various colloids alone or in combination as vehicles or binding agents. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example gelatin, gelatin derivatives (e.g., phthalated gelatin), cellulose derivatives, polysaccharides such as dextran gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds, e.g., poly(vinylpyrrolidone) acrylamide polymers or other synthetic polymeric compounds such as dispersed vinyl compounds in latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Pat. Nos. 3,142,568 of Nottorf; 3,193,386 of White; 3,062,674 of Houck, Smith and Yudelson; U.S. Pat. No. 3,220,844 of Houck, Smith and Yudelson; Ream and Fowler, U.S. Pat. No. 3,287,289; and Dykstra, U.S. Pat. No. 3,411,911; 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 Canadian Patent 774,054.

Emulsions in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk, U.S. Pat. Nos. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoy, U.S. Pat. No. 3,428,451.

Photographic emulsions of the invention can be coated on a wide variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethyleneterephthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or 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, ethylenebutene copolymers and the like.

Emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton, U.S. Pat. No. 2,960,404; fatty acids or esters such as those described in Robins, U.S. Pat. No. 2,588,765 and Duane, U.S. Pat. No. 3,121,060; and silicone resins such as those described in DuPont British Patent 955,061.

The photographic emulsion as described herein can contain surfactants such as saponin, anionic compounds such as the alkylarylsulfonates described in Baldsiefen, U.S. Pat. No. 2,600,831, fluorinated surfactants, and amphoteric compounds such as those described in Ben-Ezra, U.S. Pat. No. 3,133,816.

Photographic elements containing emulsion layers sensitized as described herein can 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. No. 2,992,101 and Lynn, U.S. Pat. No. 2,701,245.

Spectrally sensitized emulsions of the invention can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Albers et al., German Patent 972,067 and McFall et al., U.S. Pat. No. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen, German Patent 1,150,274 and Oetiker et al., U.S. Pat. No. 3,406,070.

Photographic elements containing emulsion layers sensitized according to the present invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdy, U.S. Pat. No. 3,253,921; Gaspar, U.S. Pat. No. 2,274,782; Carroll et al., U.S. Pat. No. 2,527,583 and Van Campen, U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and Jones, U.S. Pat. No. 3,282,699.

Contrast enhancing additives such as rhodium, iridium, ruthenium and combinations thereof are also useful in addition to the hydrazides.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin, U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell, U.S. Pat. No. 2,761,791 and Wynn, British Patent 837,095.

Other conventional photographic addenda such as coating aids, antistatic agents, acutance dyes, antihalation dyes and layers, antifoggants, latent image stabilizers, antikinking agents, and the like may also be present.

Although not essential in the practice of the present invention, one particularly important class of additives which can find particular advantage in the practice of the present invention is high intensity reciprocity failure (HIRF) reducers. Amongst the many types of stabilisers for this purpose are chloropalladites and chloroplatinates (U.S. Pat. No. 2,566,263), iridium and/or rhodium salts (U.S. Pat. Nos. 2,566,263; 3,901,713), cyanorhodates (Beck et al., J. Signalaufzeichnungsmaterialen, 1976, 4, 131), ruthenium and cyanoiridates.

EXAMPLES

This invention will be further illustrated with some examples. A sulfur digested silver chloroiodobromide emulsion was split into three separate containers and then finalled with either 1) a blue sensitive dye (A=#6748) or 2) a red sensitive dye (B=#6774) stabilized with a green dye (#6682) or 3) an infrared sensitive dye (C=IS-10) at pre-determined optimum levels for maximum sensitivity as a single emulsion. These then were completed by adding a polyethylene oxide compound, a wetting agent, a contrast promoter, a stabilizer and a hydrazide (1-(2'-hydroxymethylbenzoyl)-2-(n-butyl)-phenyl hydrazine) dispersion. The separately finalled emulsions were then either mixed together just prior to coating or better yet coated as separate layers at the same time with a topcoat and in-line mixed hardener (triazine). As a reference coating, an emulsion was attempted to be sensitized to all three wavelength regions at once by adding all three dyes to the one emulsion in various orders of addition.

All film samples were exposed on a laser sensitometer which can selectively expose with either an Argon ion, He-Ne or IR laser through a 0 - 3.0 density continuous tone wedge with a midrange exposure level of 5, 2 or 20 erg/cm sq at the film plane, respectively. In addition, all samples were processed through

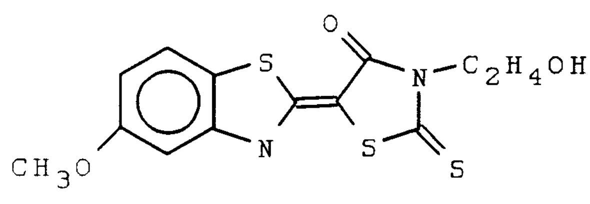
Excelerate chemistry at 97°F and 35 seconds processing time in a RA-66 processor. These materials were coated on the opposite side of 4 mil (0.1mm) PET coated with an IR AH (Infrared Anti-halo layer) and hardened with triazine hardener.

Initial attempts to sensitize only one emulsion to all three wavelength regions at once proved unsuccessful, no matter the order of dye additions (see Table I). In fact, at each wavelength region of interest, over 0.7 logE and as much as 1.0 logE in speed was lost versus the singly dyed reference emulsion controls. In addition, the contrast of this formulation was low, in fact as low as a rapid access film type contrast, seemingly indicating that the hydrazide did not trigger properly.

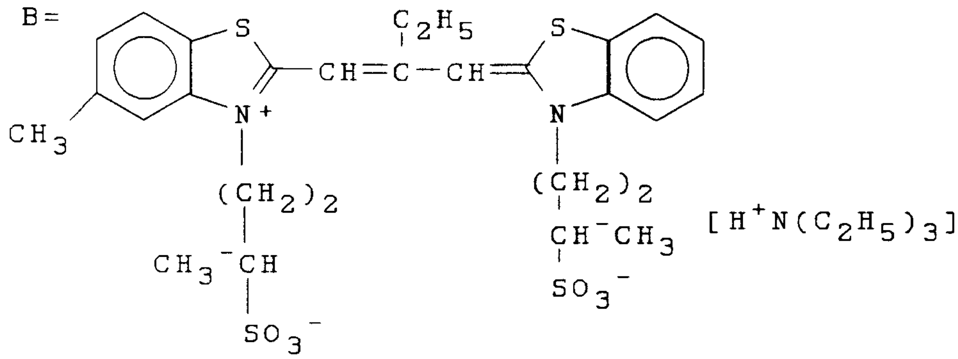
An alternate approach in which emulsions were dyed and completely finalled separately (to allow the dyes to absorb on their respective grains) before mixing together at equal parts just prior to coating, was also tried. This coating (3-Way Blend) contained the equivalent of 1.1 g/m sq of silver in the final coated film from each emulsion component (AR emulsion, HN emulsion and infrared emulsion) yet gave high Dmax's (>4.5 density), good contrast values and some loss in speed versus the single emulsion controls (see Table II). The speed loss was especially bad for the IR response, which was 1.0 logE slower than the IR control - that is to say it was 10 times slower! Apparently the IR dye is not adsorbed strongly enough to prevent it being displaced by the other dyes upon mixing all three emulsions together, even just prior to coating. This desorption may also be due to the difference in quantities of dye necessary for optimum sensitizing between the AR and HN dyes, which are added at roughly 10 times greater levels, and the IR dye.

Finally a third approach was tried which coated the 3 different wavelength emulsions in separate layers on top of each other, each layer at only 1.1 g/m sq of silver, in one multi-slot coating trial. There are 6 different possible combinations of arranging the various emulsions but only two were studied in any great detail because of earlier work showing stability problems if the IR emulsion layer was on top with this particular IR anti halation layer. The best arrangement of layers are 1) AR layer on top, IR layer on bottom, HN layer in between or 2) AR layer on top, HN layer on bottom, IR layer in between. Evaluation of these two prototypes gave no appreciable speed, Dmax or contrast losses versus the controls (see Table III, IV) for exposure to either 488 nm or 633 nm lasers while there was slight loss in speed-only to the 780 nm laser (less than 0.25 LogE for the best one). Excellent contrast, Dmin and Dmax, however, was obtained even to the IR laser exposure. These results are quite remarkable considering that each specific layer only accounts for 1.1 g/m sq of silver sensitive specifically to a particular laser wavelength (with the other layers having little or no sensitivity at all to that wavelength) which would only give a Dmax of 1.8 (predicted based on a coating weight series of the control emulsions). One can actually show that this is true by processing the Separate Layer sample in RPD chemistry (a rapid access chemistry) which does not trigger the hydrazide infectious development (see Table V). In this case, the Dmax of the Separate Layers example or the 3-Way blend sample exposed at the 633 nm region only gives a density of ~1.7. Unexpectedly, the density in the 488 nm region was ~3.3 - basically double that expected. However, upon examination of the wedge spectra of the different emulsions, it became readily apparent that the Helium-Neon sensitized emulsion has significant sensitivity at 488 nm and also contributes to the developed density at this wavelength. It was not possible to measure the IR response of these films in RPD Chemistry because of a major loss in speed for this system (such that no IR sensitivity was observed!) when the hydrazide did not trigger, apparent even for the IR control (Table V). In none of these cases, however, when the hydrazide is not present or does not trigger properly does the Dmax to any one wavelength exposure even approach the density of >4.5 seen in this invention.

A =



B =



C =

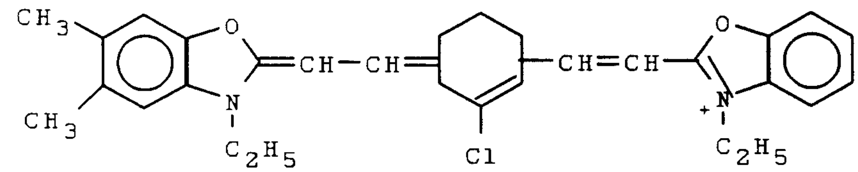


TABLE I

Coating	At 488 nm		At 633 nm		At 780 nm		g/m^2
	DMAX	REL SP	DMAX	REL SP	DMAX	REL SP	Ag
AR Control	5.06	0.00					3.30
HN Control			4.76	0.00			3.30
IR Control					4.99	0.00	3.30
Sensitized to all 3 wavelengths at once	4.97	-.96	5.03	-.68	4.97	-.88	3.30

Note - a 0.3 log E in speed difference is a factor of two change in speed
DMAX is the maximum density obtained
REL SP is the relative speed *vs* the control

TABLE II

Coating	At 488 nm		At 633 nm		At 780 nm		g/m^2
	DMAX	REL SP	DMAX	REL SP	DMAX	REL SP	Ag
AR Control	4.95	0.00					3.30
HN Control			4.61	0.00			3.26
IR Control					4.92	0.00	3.30
3-WAY BLEND	5.04	-.25	4.68	-.43	4.27	-.99	3.28

TABLE III

Coating	At 488 nm		At 633 nm		At 780 nm		g/m²
	DMAX	REL SP	DMAX	REL SP	DMAX	REL SP	Ag
AR Control	4.95	0.00					3.30
HN Control			4.61	0.00			3.26
IR Control					4.92	0.00	3.30
AR layer on top of HN layer which is on top of IR layer	4.89	+.06	4.83	-.03	4.78	-.21	3.09
AR layer on top of IR layer which is on top of HN layer	5.08	+.10	4.73	-.05	4.80	-.29	3.24

TABLE IV

SAMPLE	SENSI	LASER EXPOSURES at 488 nm	at 633 nm	at 780 nm
		ARGON ION	HE-NE	INFRARED
	DMIN	0.037	0.041	0.041
Individual	DMAX	4.95	4.61	4.92
CONTROLS	SP. 1	1.12	0.80	0.63
	THETA A	1.79	2.44	2.47
	THETA C	8.6	12.8	17.4
	DMIN	0.040	0.040	0.040
Best	DMAX	4.89	4.83	4.78
SEPARATE LAYERS	SP.1	1.18	0.77	0.42
Approach	THETA A	1.96	2.73	2.88
	THETA C	10.8	16.6	15.3

NOTE: Sp. 1 is the speed point at 0.2 density value above Dmin level.
Theta A is a measure of toe contrast.
Theta C is a measure of shoulder contrast.

TABLE V

WEDGE SPECTRA DENSITY*

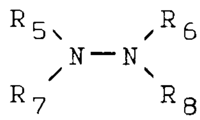
COATING	DMAX at 488 nm	DMAX at 633 nm	DMAX at 780 nm	Ag(g/m²)
AR CONTROL	5.25 2.95			3.30 1.60
HN CONTROL		4.75 2.51		3.26 1.60
IR CONTROL			—	
3-WAY BLEND	3.25	1.75	—	3.28
SEPARATE LAYERS	3.35	1.70	—	3.24

* DMAX OBTAINED IN RPD CHEMISTRY FOR 10 SECOND EXPOSURES

To achieve the benefits of this invention, a hydrazine compound (hydrazide) has to be present during development of the exposed element.

The hydrazine compound (hydrazide) can be incorporated in the photographic element or in the developing solution or both in the developing solution and in the photographic element. It is preferred to be in at least the element itself.

Hydrazine and any water soluble hydrazine derivatives are effective in increasing contrast when incorporated in the developing solution in combination with the diarylmethanol compound incorporated in the photographic element. Preferred hydrazine derivatives to be used in the developing solution of this invention include compounds of formula (I):



(I)

wherein R_5 is an organic radical and R_6, R_7, and R_8 each are hydrogen or an organic radical. Organic radicals represented by R_5, R_6, R_7, and R_8 include hydrocarbon groups, such as an alkyl group, an aryl group, an arylalkyl group and an alicyclic group and such groups can be substituted with substituents such as alkoxy groups, carboxy groups, sulfonamido groups and halogen atoms.

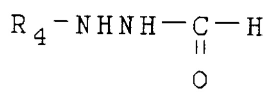
Other examples of hydrazine derivatives, which can be incorporated in the developing solutions, are hydrazides (including aryl hydrazides and formyl hydrazides), acyl hydrazines, semicarbazides, carbohydrazides and aminobiuret compounds.

Specific examples of hydrazine derivatives, which can be incorporated in the developing solutions of the present invention, are disclosed in U.S. Patent Specification 2,419,575.

In a preferred form of this invention, the hydrazine compound is incorporated in the photographic element, for example, in a silver halide emulsion layer or in a hydrophilic colloidal layer, preferably a hydrophilic colloidal layer adjacent to the emulsion layer in which the effects of the hydrazine compound are desired. It can, of course, be present in the photographic element distributed between the emulsion and the hydrophilic colloidal layers, such as a subbing layer, interlayers and protective layers.

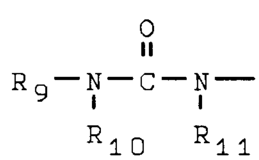
Hydrazine compounds suitable to be incorporated into the photographic element according to the present invention are disclosed in G. B. Patent Specification 598,108 and in U.S. Patent Specification 2,419,974; they include the water soluble alkyl, aryl and heterocyclic hydrazine compounds, as well as the hydrazide, semicarbazide and aminobiuret compounds.

Particularly preferred hydrazine compound, for use according to this invention incorporated in the photographic element, are the formylhydrazine compounds corresponding to the formula (II):



(II)

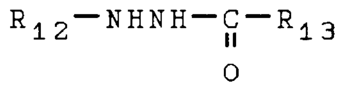
wherein R_4 represents a substituted or unsubstituted aromatic group. Examples of aromatic groups represented by R_4 include a phenyl group and a naphthyl group. Such aromatic groups may be substituted with one or more substituents which are not electron attracting, such as straight or branched-chain alkyl groups (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, n-octyl, n-hexyl, tert-octyl, n-decyl, n-dodecyl, etc.), arylalkyl groups (e.g., methoxy, ethoxy, 2-methyl-propyloxy, etc.), amino groups which are mono- or disubstituted with alkyl groups, acylaminoaliphatic groups (e.g., acetylamino, benzoylamino, etc.), etc., as disclosed in U.S. Patent 4,168,977 and a CA Patent 1,146,001. Such aromatic groups may also be substituted with a ureido group of formula (III):



(III)

R_9 and R_{10} (which may be same or different) each represents hydrogen, a aliphatic group (such as a straight or branched-chain alkyl groups, a cycloalkyl group, a substituted cycloalkyl group, an alkenyl group and an alkynyl group), an aromatic group (such as a phenyl group and a naphthyl group) or a heterocyclic group; R_{11} represents hydrogen or an aliphatic group (such as those listed above) as described in U.S. Patent 4,323,643.

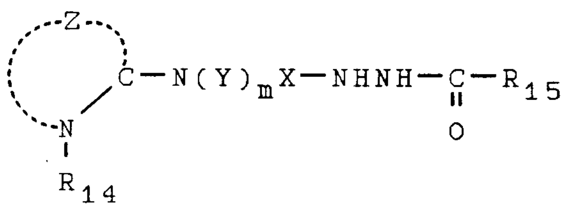
Other hydrazine compounds, for use according to this invention, incorporated in the photographic element are those represented by the formula (IV):



(IV)

wherein R_{12} represents the same aromatic group of the formula above and R_{13} represents an alkyl group have 1 to 3 carbon atoms, which may be a straight or branch-chain alkyl (e.g., methyl, ethyl, n-propyl and isopropyl) or a phenyl group. The phenyl group may be substituted with one or more substituents which preferably are electron attracting groups, such as halogen atoms (chlorine, bromine, etc.), a cyano group, a trifluoromethyl group, a carboxy group or a sulfo group, etc. Specific examples of hydrazine compound represented by the formula above are disclosed in U.S. Patent 4,224,401.

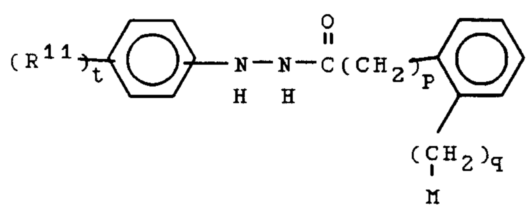
Still other examples of hydrazine compounds, for use according to this invention incorporated in the photographic element, are those corresponding to the formula (V):



(V)

wherein R_{14} represents hydrogen, an aliphatic group which may be substituted; Y represents a divalent linking group; m represents 0 or 1; X represents a divalent aromatic groups (such as for example a phenylene group, a naphthylene group and the analogous substituted groups thereof); R_{15} represents a hydrogen atom, an aliphatic groups which may be substituted and Z represents a non metallic atom group necessary to form a 5- or a 6-membered heterocyclic ring. Specific examples of hydrazine compounds represented by the formula above are disclosed in U.S. Patent 4,272,614.

A preferred class of compounds for use in the invention has the formula (VI):



(VI)

in which:

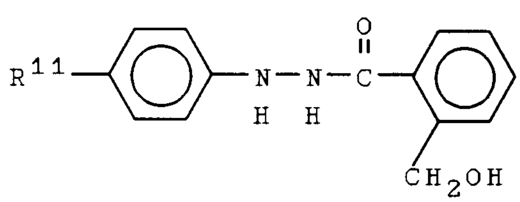
p and q are independently selected from 0 or 1 such that $(p + q) = 1$

R^{11} is as defined previously above

M is NH_2 or OH

A compound of the above formula in which M is OH, p is zero and t is zero is known; the remaining compounds are novel and form a further aspect of this invention.

Particularly preferred compounds of the invention are the formula (VII):



(VII)

in which: R^{11} is as defined above.

Such hydrazine compounds can be incorporated in the photographic element using various methods well-known in the photographic art, the most common being the method of dissolving the hydrazine derivatives in a high boiling crystalloidal solvent and dispersing the mixture in the emulsion, as described for example in U.S. Patent 2,322,027.

Hydrazine compounds incorporated in the developing solution in the practice of this invention are effective at low concentrations. For example, hydrazine compounds give useful results in the developing solution in a quantity of about 0.001 moles per liter to about 0.1 moles per liter, more preferably in a quantity from about 0.002 to about 0.01 moles per liter. Hydrazine compounds incorporated in the photographic element are typically employed in a concentration ranging from about 5 x 10^{-4} to about 5 x 10^{-2} moles per mole of silver and preferable in a quantity from about 8 x 10^{-4} to about 8 x 10^{-3} moles per mole of silver.

Contrast promoting agents such as alkanolamines and diarylcarbinol compounds, preferably the diarylcarbinols such as diarylmethanol compounds described herein, are incorporated into the developer bath or preferably the photographic element prior to contact with the whole developer solution and preferably prior to the exposure of the photographic element itself, such as for example, when the diarylcarbinol compound is introduced into the element prior to or contemporaneously with the coating of the emulsion layer. For example, they can be incorporated in the silver halide emulsion layer of the element or in a hydrophilic colloidal layer of the element, particularly a hydrophilic colloidal layer adjacent to the emulsion layer in which the effects of the diarylcarbinol compounds are desired. They can, for instance, be present in the photographic element distributed between the emulsion and they hydrophilic colloidal layers, such as for instance a subbing layer, interlayers and protective layers.

Parameters to take into proper account are solubility and boiling points of the diarylcarbionol compounds of the present invention. Said compounds are to be substantially soluble in water or soluble in water miscible solvents (by "substantially soluble" in water is meant that they are to be soluble in water in a quantity of at least 1% by weight and by "soluble" in water-miscible solvents it is meant that they are to be soluble in water miscible solvents in a quantity of at least 5% by weight) in order to introduce them into the aqueous coating compositions used to form the layers of the photographic elements according to the present invention. Said diarylcarbinol compounds are required to have a sufficiently high boiling point not to evaporate during drying of the layer forming coating composition. Said boiling points are preferably higher than 150 ° C, more preferably higher than 200 ° C.

Specific examples of diarylcarbinol compounds according to this aspect of the invention include the following:

1) diphenylmethanol (a.k.a. benzhydrol)
2) 4,4'-dimethoxydiphenylmethanol
3) 4,4'-dimethyldiphenylmethanol
4) 2,2'-dibromodiphenylmethanol
5) 4,4'-dibromodiphenylmethanol
6) 2,2'-dinitrodiphenylmethanol
7) 4,4'-dinitrodiphenylmethanol
8) 2,3'-dimethoxydiphenylmethanol
9) 2,4'-dihydroxydiphenylmethanol
10) 4-methyldiphenylmethanol
11) 4-ethyldiphenylmethanol
12) 2,2',4,4'-tetramethyldiphenylmethanol

The diarylcarbinol compounds are preferably used in the present invention, when incorporated into the photographic element in amounts from about 10^{-4} to about 10^{-1} mole per mole of silver, more preferably in an amount from about 10^{-3} to about 5 x 10^{-2} mole per mole of silver.

According to the process of the present invention, the image-wise exposed silver halide photographic element can be processed with a stable aqueous alkaline developing solution to produce a high contrast negative image. This contrast is the slope for the straight line portion of the characteristic sensitometric curve (referred to as "average contrast") and is measured between two points located at densities of 0.10 and 2.50 above fog. Averages contrast higher than 10 can be obtained according to this invention by developing an image-wise exposed element in the presence of a hydrazine compound.

The dihydroxybenzene developing agents employed in the aqueous alkaline developing solution for use in the practice of this invention are well-known and widely used in photographic processings. The preferred developing agent of this class is hydroquinone. Other useful dihydroxybenzene developing agents include chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, tolylhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhydroquinone, 2,3-dibromohydroquinone, 1,4-dihydroxy-2-acetophenone-2,5-dimethylhydroquinone,2,5-diethylhydroquinone, 2,5-di-p-phenethylhydroquinone, 2,5-dibenzoylhydroquinone, 2,5-diacetaminohydroquinone and the like.

The 3-pyrazolidone developing agents employed (and which may or may not be present in the aqueous alkaline developing solution or the emulsion) in the practice of this invention are also well known and widely used in photographic processings. The most commonly used developing agents of this class are 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone and 1-phenyl-4,4-dihydroxymethyl-3-pyrazolidone. Other useful 3-pyrazolidone developing agents include:
1-phenyl-5-methyl-3-pyrazolidone,
1-p-aminophenyl-4-methyl-4-propyl-3-pyrazolidone,
1-p-chlorophenyl-4-methyl-4-ethyl-3-pyrazolidone,
1-p-acet-amidophenyl-4,4-diethyl-3-pyrazolidone,
1-p-Beta-hydroxy-ethylphenyl-4,4-dimethyl-3-pyrazolidone,
1-p-hydroxy-phenyl-4,4-dimethyl-3-pyrazoidone,
1-p-methoxyphenyl-4,4-diethyl-3-pyrazoidone,
1-p-tolyl-4,4-dimethyl-3-pyrazolidone, and the like.

The preferred aqueous alkaline photographic developing composition for use in the practice of this invention contains a sulfite preservative at a level sufficient to protect the developing agents against aerial oxidation and thereby assure good stability characteristics. Useful sulfite preservatives include sulfites, bisulfites, metabisulfites and carbonyl bisulfite adducts. Typical examples of sulfite preservatives include sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite, sodium formaldehyde bisulfite salt and the like. Also ascorbic acid is a known preservative agent against aerial oxidation of the developer for use in the bath according to this invention.

The aqueous alkaline developing solutions for use in the practice of this invention can vary widely with respect to the concentration of the various ingredients included therein. Typically, the dihydroxybenzene developing agent is used in an amount of from 0.040 to about 0.70 moles per liter, more preferably in an amount of from 0.08 to about 0.40 moles per liter; the 3-pyrazolidone developing agent is used in an amount of from about 0.001 to about 0.05 moles per liter, more preferably in an amount of from about 0.005 to about 0.01 moles per liter; the sulfite preservative is used in an amount from about 0.03 to about 1.0 moles per liter, more preferably in an amount from about 0.10 to about 0.70 moles per liter.

In contrast with "lith" developers which require a low level of sulfite ions, the developing solutions of this invention can utilize higher levels of sulfite ions, and thereby achieve the advantages of increased stability, since a higher level of sulfite ions provides increased protection against aerial oxidation.

In carrying out the method of this invention, it is preferred to use an organic antifogging agent to minimize fog formation in the processed element. The organic antifogging agent can be incorporated in the photographic element or can be added to the developing solution or can be both incorporated in the photographic element and added to the developing solution. According to the present invention, it has been found that more preferred organic antifogging agents for specific use in the developing solutions are benzotriazole and/or a benzimidazole antifogging agent, which proved to have beneficial effects on increasing contrast. Useful compounds are both substituted and unsubstituted benzotriazole and benzimidazole compounds, with the provision that electron withdrawing substituents at least as strong as nitro groups are excluded.

Claims

1. A black-and-white silver halide photographic element comprising a substrate having at least two silver halide emulsion layers thereon, the total weight of silver on said substrate being less than 5.0 g/m^2, said at least two silver halide emulsions being spectrally sensitized to at least two different wavelengths of the electromagnetic spectrum which differ by at least 50 nm, and at least one of said silver halide emulsion layers containing a contrast enhancing hydrazide.

2. A black-and-white silver halide photographic element comprising a substrate having at least three silver halide emulsion layers thereon, each of said at least three silver halide emulsion layers being spectrally sensitized to different wavelengths of the electromagnetic spectrum which differ from each other by at least 50 nm, and the total weight of silver on said substrate being less than 5.0 g/m^2, at least one of said silver halide emulsion layers containing a contrast enhancing hydrazide.

3. The element of Claim 1 wherein one of said at least two different wavelengths is within the infrared region of the spectrum and the emulsions layer spectrally sensitized to the infrared is not the outermost silver halide emulsion layer from said support.

4. The element of Claim 2 wherein one of said different wavelengths is within the infrared region of the spectrum and the silver halide emulsion spectrally sensitized to the infrared is not the outermost silver halide emulsion layer from said support.

5. The element of Claim 1 having one emulsion spectrally sensitized to a wavelength between 470 and 500 nm.

6. The element of Claims 1, 2 or 3 having one emulsion spectrally sensitized to a wavelength between 600 and 680 nm.

7. The element of Claims 1, 2 or 3 having one emulsion spectrally sensitized to a wavelength between 700 and 1,300 nm.

8. The element of Claim 6 having one emulsion spectrally sensitized to a wavelength between 470 and 500 nm.

9. The element of Claim 7 having one emulsion spectrally sensitized to a wavelength between 600 and 680 nm.

10. A process for making a black-and-white silver halide photographic element comprising providing at least two separate black-and-white silver halide emulsions, separately spectrally sensitizing each of said silver halide emulsions to different wavelengths of the electromagnetic spectrum which differ by at least 50 nm, and coating said emulsions onto a support layer to form said element, said element additionally containing a contrast enhancing hydrazide in reactive association with said silver halide emulsion layers, and wherein said spectrally sensitized emulsions are coated onto said support as separate layers.