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3,752,670

PHOTOGRAPHIC FILM ELEMENT AND METHOD FOR OBTAINING PHOTOGRAPHIC RECORDS OF WATER-SUBMERGED OBJECTS

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No Drawing. Filed Dec. 29, 1971, Ser. No. 213,813

Int. Cl. G03c 1/14, 7/00

U.S. Cl. 96—74

23 Claims

ABSTRACT OF THE DISCLOSURE

A color photographic element comprising a blue-sensitized silver halide emulsion layer having a maximum light absorption within about 480–500 nm. and having substantially no absorption above about 510 nm., containing a benzo- or naphtho-thia-, oxa- or selenacarbo-cyanine salt as a blue spectral sensitizer dye, an inner green-sensitized emulsion layer responsive to light within about 525–590 nm. and an intermediate filter layer that filters light in the range of about 400–520 nm.; and also a method for improving photographic recordal of objects submerged in water by using such photographic elements.

This invention relates to a new color photographic element suitable for recordal of objects submerged in an aqueous medium such as in sea water.

Because of the increased ecological, scientific, economic and recreational interest now being directed to the undersea world, it is both convenient and necessary that color photographic means be provided for recording and interpreting this world both from within and from outside.

In order to achieve this goal, however, it is necessary to solve a number of difficult technical problems, some of which are unique to underwater photography and others of a more general type.

In obtaining color photographic records of underwater subjects, for instance, it has been found that the light-scattering, the light-absorbing and the light-transmitting properties of water vary substantially depending upon (1) the type of water (i.e., pure water, sea water, the less saline coastal bay water, etc.), (2) the depth and distance of the water to be penetrated photographically, and (3) the wave length of the light to be recorded. It is noted, for instance, that the percentage of light transmitted through pure water at a depth of about 10 meters will vary from about 85% to about 55% in the 470–570 nm. range, while a corresponding transmission at 100 meters will vary from about 20% to .3%. Similar, although far from identical variations in light transmission are found for ocean and bay water (ref. Journal of the American Society of Photogrammetry; vol. XXXVI, No. 2 (1970), pp. 164–172).

It has been noted that relatively small amounts of light are expected to impinge upon a water penetration film due, mainly, to a substantial amount of light absorption by water. A high ASA rating is not a complete answer, however, since the range of maximum average light penetration of water significantly overlaps an area of the visible spectrum in which various light-scattering effects occur. For the most part this interference is due to suspended particulate matter in water and air. A good water penetration film, therefore, must favor the higher visible blues.

Ease in processing is another important consideration, since large volumes of a water penetration film are normally required to completely record an area of sea bottom.

Mere recognition of the above facts and the technical

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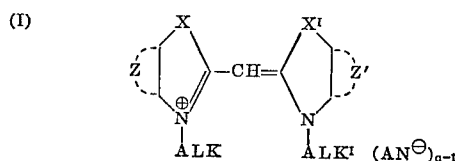
burdens which they imply, however, does not constitute disclosure of a way to obtain the desirable characteristics in workable water penetration film.

It is an object of the present invention to provide a photographic element sensitive to the area of maximum light transmission through water, particularly in the higher blue wavelengths, to permit the exclusion of light interference while maintaining a sufficient amount of speed and differentiation in the upper blue and the green spectrum.

It is a further object of the present invention to provide a multilayer photographic element which can be easily produced and developed using present day photographic concepts and techniques and to obtain records which are easily demonstrated.

It is a still further object of the present invention to obtain water penetration film having improved resolution and speed when exposed above or below the water.

The above objects are achieved by utilizing a photographic element comprising a support layer having coated thereon two light-sensitive emulsion layers comprising an inner green-sensitized silver halide emulsion layer responsive to light having a wavelength within about 525–590 nm. and a blue-sensitized silver halide emulsion layer having a maximum light absorption wavelength within about 480–500 nm. and having substantially no light absorption above about 510 nm., the latter blue-sensitized emulsion layer being sensitized with at least one compound having the formula:



wherein

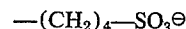
Z is defined as carbon and hydrogen atoms which, in combination with X, complete a benzothiazole radical, a benzoselenazole radical, a benzoxazole radical, a naphthothiazole radical or a naphthoselenazole radical;

X is defined as —O—, —S—, or —Se—;

Z' is defined as the carbon and hydrogen atoms which, in combination with X' complete a quinoline radical when X and Z in combination define a benzoxazole radical, Z' being otherwise defined as the carbon and hydrogen atoms which in combination with X' complete a benzothiazole radical, a benzoselenazole radical, a naphthothiazole radical or a naphthoselenazole radical;

X' is defined as —S—, —Se—, or the carbon and hydrogen atoms required to complete a quinoline radical;

ALK and ALK' individually represent an alkyl group of 1–15 carbons including a sulfoalkyl group and a carboxyalkyl group such as —CH₃, —C₁₅H₃₁,



and —(CH₂)₄—COO[⊖];

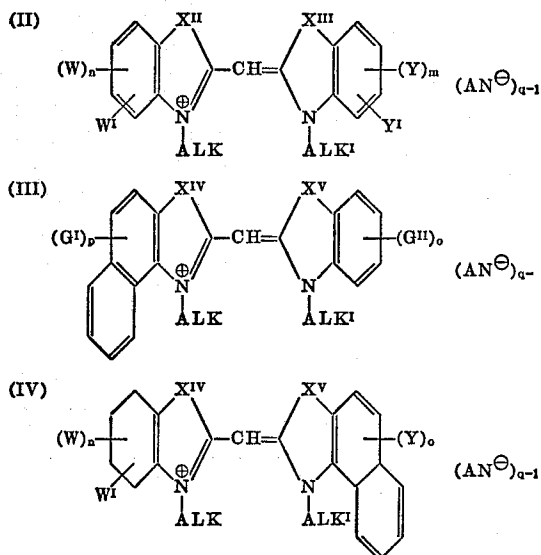
AN is an acid anion group such as a chloride, bromide, iodide, thiocyanate, sulfamate, methylsulfate, ethylsulfate, perchlorate, p-toluenesulfonate etc.; and

q represents an integer of 1–2 such that q is 1 when at least one of ALK or ALK', is defined as a sulfoalkyl group or a carboxyalkyl group; plus

a light filter layer positioned between the green- and blue-sensitized emulsion layers, filtering light having a wavelength in the range of about 400–520 nm.; the green- and blue-sensitized emulsion layers each containing at least one photographic coupler capable of forming a dye with oxidized aromatic primary amino color developing agents, the dyes found in the respective emulsion layers being different subtractive primary colors.

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More specifically, the above photographic element can utilize a blue-sensitized emulsion layer containing at least one blue-sensitizing dye of the formulae



wherein

W and Y are individually defined as a halo group such as chloro or iodo, an alkoxy group, including alkoxy of 1-20 carbon atoms such as methoxy, isopropoxy, and eicosyloxy, an aryl group such as a phenyl group or a naphthyl group exemplified by phenyl, chloro phenyl, methyl phenyl, and naphthyl;

W^I, Y^I, G^I and G^{II} are individually defined as hydrogen, a halo group such as chloro or fluoro or an alkyl group, particularly an alkyl group of 1-20 carbon atoms such as methyl and eicosyl;

X^{II} is defined as —S—, —Se— or —O—;

X^{III} is defined as the carbon and hydrogen atoms required to complete a quinoline radical when X^{II} is —O— and otherwise defined as —S— or —Se—;

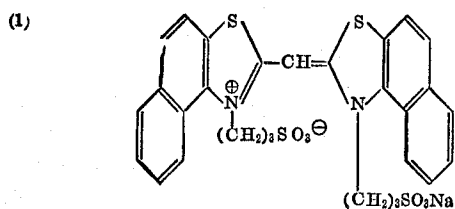
X^{IV} and X^V are individually defined as —S— or —Se—; m, n and o are integers of 0-3, preferably 0-2; p is 0-1; and

ALK, ALK^I, AN and q are defined as above.

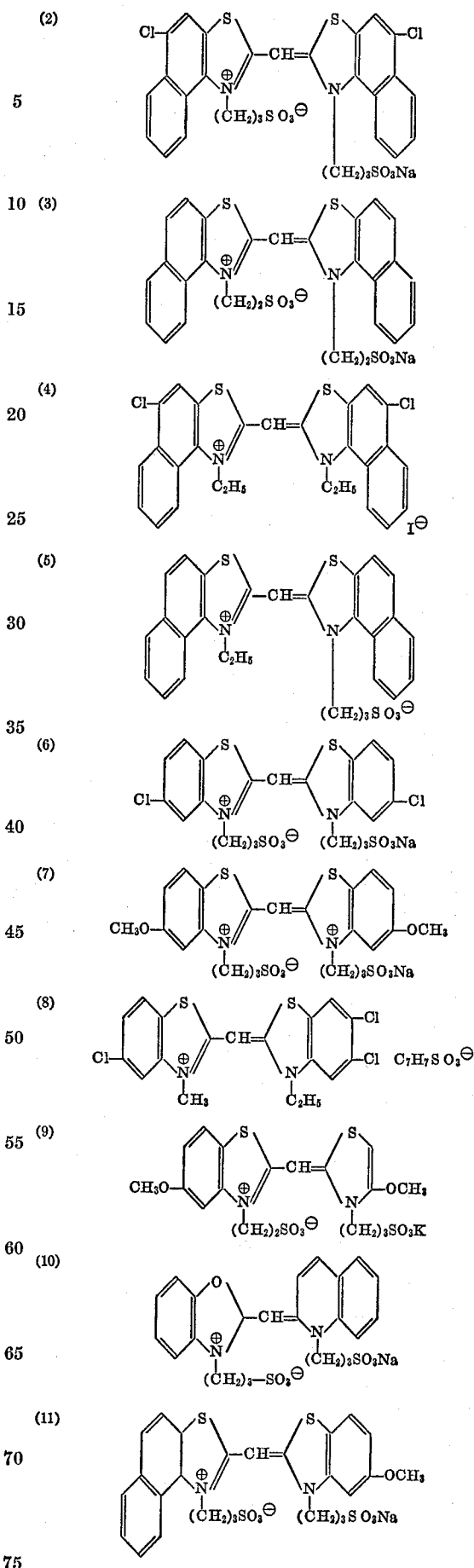
Of particular interest for purposes of the present invention are the dye sensitizers of Formula I in which X and Z in combination is a benzothiazole or a benzoselenazole radical containing a 5- or 6-lower alkoxy ring substituent of 1-8 carbons such as a methoxy or octyloxy, naphthothiazoles such as a naphtho [1,2-d] thiazole, a naphtho [2,1-d] thiazole, a naphtho [2,3-d] thiazole, also a corresponding unsubstituted or chloro-, alkyl- or aryl-substituted benzoxazole or a naphthoselenazole radical; and in which

Z' is a benzothiazole or a benzoselenazole radical containing a 5- or 6-methoxy ring substituent, a naphthothiazole radical or a naphthoselenazole radical as defined above for Z, and a 2-quinoline radical when Z is defined as a benzoxazole radical.

Specific blue-sensitizer dyes within the scope of the present invention include:

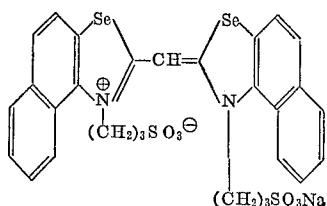


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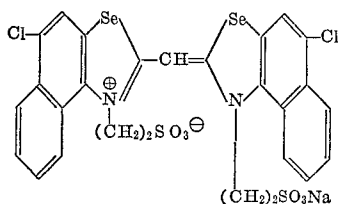


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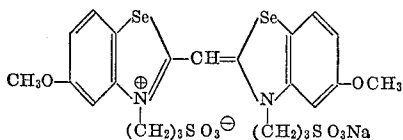
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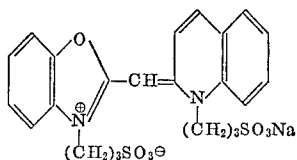
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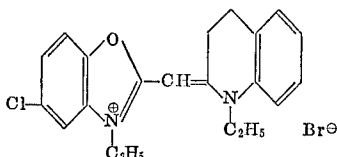
(14)



(15)



(16)



A satisfactory photographic element for water penetration purposes can include, for instance, the following main components:

(A) A support layer such as cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, poly(ethylene terephthalate) film, polyethylene film, polypropylene film and related films of resinous materials as well as paper, polyethylene coated paper, glass, and others. The terms include paper or other flexible fibrous material which can be partially acetylated or coated with baryta or some other hydrophobic film or surface which repels and does not absorb or adsorb water. A support layer having a hydrophobic surface can also include hydrophobic resin layers which have been electron bombarded as described, for instance, in British Pats. 971,058, 1,060,526 and U.S. Pats. 2,864,755 and 2,864,756 to improve adhesion of hydrophilic colloid layers coated over them. Such resin layers or films may be either self-supporting or may be coated over another support layer. Specific supports having useful hydrophobic surfaces include polyethylene terephthalate films electron-bombarded to have a contact angle less than 45° (U.S. Pat. 3,220,842), an electron-bombarded surface comprising a chromium halide (U.S. Pat. 3,117,865), or electron-bombarded hardened gelatin coated papers (Belgian Pat. 671,661), etc. The support layer may also contain various functional additives such as titanium dioxide, zinc oxide and silica as suggested in U.S. Pats. 2,992,101 and 2,701,245, and anti-static agents as described, for instance, in U.S. Pat. 3,253,922.

(B) An antihalation layer such as a gray colloidal silver dispersed in gelatin or a dye-containing gelatin, starch, etc., as described, for instance, in Glafkides "Photographic Chemistry," volume 1, pages 470-471, Arrowsmith Ltd., 1958, is typically utilized in accordance with usual practice.

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(C) The present photographic elements contain a green-sensitized silver halide emulsion layer which is responsive to light at about 525-590 nm. and preferably contains at least two coupler compounds such as a mixture of cyan and yellow dye-producing couplers such as a phenolic, α -naphtholic and open-chained ketomethylene type, or suitably, these couplers individually, or a magenta dye-producing coupler such as a 5-pyrazolone magenta dye-forming coupler. This emulsion layer also contains one or more green-sensitizing dyes such as one or more carbocyanine dyes of the type disclosed and prepared, for instance, in U.S. Pats. 2,739,149 of Van Lare and 3,397,060 of Schwan et al., having a $\lambda_{\max}$ at about 550 nm.

(D) The present photographic elements contain a filter layer, preferably one or more dyes in the form of a gelatin filter which absorbs light at about 400-520 nm., particularly 500-520 nm.; suitable filter dyes for the purpose are disclosed, for instance, in U.S. Pat. 3,247,127 (ref. Example 7), and French Pat. 1,359,683 (dye #6).

(E) The present photographic elements contain a blue-sensitized silver halide emulsion layer containing at least one blue spectral sensitizing dye of the class defined in Formula I which has no substantial light absorption above 510 nm. and a maximum absorption range of about 480-500 nm.; this emulsion layer contains at least one coupler that forms a dye of a different subtractive primary color than that formed from the coupler(s) in the green-sensitized emulsion layer, preferably at least one magenta dye-forming coupler of the 5-pyrazolone type, or suitably, at least one cyan and one yellow dye-producing coupler of the phenolic, α -naphtholic and open-chained ketomethylene type in the event that the green-sensitized emulsion layer (C) contains a magenta dye-forming coupler.

Both the green-sensitized emulsion and the blue-sensitized emulsions described above can include coarse, regular, or fine grain silver halide crystals or mixtures thereof such as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide and mixtures thereof. Suitable emulsion components are further generally described, for instance, in "The Photographic Journal," volume LXXIX, May 1939, pages 330-338; "Journal of Photographic Science," volume 12, #5, September/October 1964, pages 242-251, and also in U.S. Pats. 2,184,013, 2,456,953, 2,541,472, 2,563,785, 2,592,250, 2,996,382, 3,367,778 and 3,501,307. The dye-forming couplers useful in the present invention can be any of the conventional non-diffusible couplers that form non-diffusible dyes when reacted with oxidized aromatic primary amino color developing agents such as p-phenylenediamines and p-aminophenols. Suitable couplers used in the green- and blue-sensitive emulsion layers can include two- and four-equivalent magenta, cyan, or yellow dye-producing couplers of the type exemplified, for instance, in U.S. Pats. 2,453,661, 2,449,966, 2,474,293, 2,521,908, 2,801,171, 2,895,826, 2,908,573, 3,311,476, 3,408,194, 3,476,563, 3,152,896 and 3,062,653.

Ballasted or non-diffusible couplers within the scope of the present invention are conveniently incorporated within gelatin, colloidal albumin, cellulose derivatives or synthetic resins, as described, for instance, in U.S. Pat. 2,286,215 or 2,327,808, water-soluble ethanol amine cellulose acetates as described in U.S. Pat. 2,322,085, also suitable polyacrylamides having a combined acrylamide content of 30-60% and a specific viscosity of .25-1.5 on an imidized polyacrylamide of similar acrylamide content and viscosity such as described in U.S. Pat. 2,541,474; into zein as described in U.S. Pat. 2,563,791; into a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in U.S. Pat. 2,768,154, or one containing cyano-acetyl groups, exemplified by vinyl alcohol-vinyl cyanoacetate copolymers as described in U.S. Pat. 2,808,331; into a polymeric material from a

protein polymerisate or into a saturated acylated polymer with a monomer having a vinyl group described in U.S. Pat. 2,852,382.

(F) One or more gelatin spacer layers can also be included between the blue- and the green-sensitized emulsion layers, such as between a light-sensitive emulsion layer and filter layer (D).

(G) A protective water-permeable overcoat layer can be used, and includes such hydrophilic materials as gelatin, poly-N-vinyl lactam, gum arabic, hydrophilic copolymer of N-acrylaminoalkyl betain (ref. U.S. Pat. 2,833,650), cellulose ethers and esters, alkali soluble polyvinyl phthalate (ref. U.S. Pat. 2,798,004); also water-soluble polymers having varying degrees of solubility, such as polyvinyl alcohol (optimally with surfactant), polyvinyl pyrrolidone polyalkylene oxides, polyvinyl alcohol and its derivatives such as partial esters, ethers and acetals exemplified by hydrolyzed polyvinylacetate, polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl sodium o-sulfobenzaldehyde acetal, polyvinyl disodium 2,4-disulfobenzaldehyde acetal; and water-soluble copolymers and interpolymers exemplified by copoly(methyl vinyl ether/maleic anhydride), copoly(acrylic acid/methacrylic acid ethyl estermaleic anhydride) and copoly (maleic anhydride/acrylic acid/vinyl acetate). The overcoat may conveniently contain aldehyde scavenger such as described, for instance, in U.S. Pats. 3,236,652, 3,287,134, 3,220,839, 2,403,927, and British Pat. 623,448, and other ingredients such as buffering agents (e.g., an acidic or basic material), and ultra-violet light absorbers such as 2,2'-di-hydroxy 4,4'-dimethoxybenzophenone, 4,4'-dimethoxybenzophenone, 4,4'- diazido - stilbene - 2,2'-disulfonic acid sodium salt, and sodium-(α -phenylhydrazone).

In addition, the silver halide emulsions used in water penetration film within the present invention can contain supplemental chemical sensitizers such as sulfur, selenium or tellurium compounds in accordance with techniques described, for instance, in U.S. Pats. 2,399,083, 3,297,447 and 3,297,446. Other useful addenda include development modifiers such as described in U.S. Pats. 2,886,437, 3,046,134 and 3,297,540, also antifoggants and stabilizers such as described, for instance, in U.S. Pats. 2,131,038, 2,403,927, 2,694,716, 2,728,663, 2,886,437, 3,236,652, 3,287,135 3,220,839, 2,566,263 and 2,597,915.

Blue spectral sensitizer dyes of the type used in the present invention can be prepared, for instance, in accordance with U.S. Pats. 2,503,776 of Sprague, as demonstrated in Examples 3, 5 and 14. A useful concentration or sensitizing amount of such a dye can vary from about 5-100 mg./liter of flowable emulsion, although widely varying amounts can be used in accordance with usual practice. The green-sensitized emulsion layer described above can usefully contain about the same concentration of green sensitizing dye (ref. U.S. Pats. 2,739,149, 3,397,060).

The cyan, magenta and yellow dye-forming couplers dispersed into layers (C) and (E) of the above-defined invention are used in a concentration range of about 25-500 mg./mole of silver in the emulsion layer.

Such couplers are conveniently dissolved into high-boiling and/or low-boiling coupler solvents, then dispersed into a gelatin solution, set, noodled, washed and then melted and combined with a light-sensitive gelatin emulsion layer in the manner described, for instance, in U.S. Pats. 2,949,360, 2,801,171, 2,304,939 and 2,322, 827.

Photographic elements within the present invention are preferably imagewise exposed through an additional filter which can be either a taking filter such as a Wratten No. 3 filter attached to the camera or in the form of a filter dye-containing layer such as the overcoat layer or additional gelatin layer coated external to the blue sensitized layer. Such an additional filter excludes ultraviolet light and particularly blue light in the lower portion of the visible blues below 480 nm. Suitable filters generally absorb at least

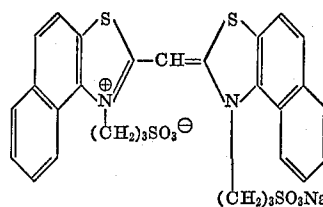
about 80% of the ultraviolet and shorter blue light up to 480 nm. Filter dyes useful for this purpose are exemplified by bis[1,3-dithylbarbituric acid (5)] methineoxonol ($\lambda_{\max}$ 420), and bis[3 - phenyl-2-isoxazolin-5-one (4)] methineoxonol, pyridine salt ($\lambda_{\max}$ 425) as disclosed in J.A.C.S. 73, 5332 (1951). Other dyes having similar absorption properties are also useful for this purpose.

This invention is further described, although not limited by the following examples:

EXAMPLE I

A test film strip of camera speed and identified as (A), is prepared by coating a transparent cellulose acetate support layer with the following:

- (1) a gray colloidal silver antihalation layer dispersed in gelatin and coated at 31 mg. silver/ft.²;
- (2) a gelatin subbing layer;
- (3) a green-sensitized silver bromoiodide gelatin emulsion layer (6.3 mole percent iodide) sensitized to light having a wavelength within 525-590 nm., coated at 240 mg. silver/ft.² and 440 mg. gelatin/ft.² into which is dispersed a coupler-gelatin dispersion of the cyan and yellow dye-forming couplers:
 - 5 - [α - (2,4 - di-tert-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol (48 mg./ft.²),
 - 1 - hydroxy - 2 - [Δ -(2,4-di-tert-amylphenoxy)-N-butyl]-naphthamide (48 mg./ft.²), and
 - α - pivalyl - α (4 - carboxyphenoxy)-2-chloro-5-[α -(3-N - pentadecylphenoxy)butyramido] - acetanilide (213 mg./ft.²),
- (4) a gelatin interlayer;
- (5) a gelatin filler layer which absorbs light from 400-520 nm. (100 mg. gelatin/ft.²);
- (6) a gelatin interlayer;
- (7) a blue-sensitized silver bromoiodide gelatin emulsion (6.3 mole percent iodide) coated at 170 mg. silver/ft.² and 245 mg. gelatin/ft.² into which is dispersed a coupler-gelatin dispersion of the magenta dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-[3-(α -(3-pentadecylphenoxy) - butyramido) - benzamido] - 5-pyrazolone (190 mg./ft.²), and also includes a blue-sensitizing dye of the formula



- (190 mg./ft.²); and
- (8) a protective gelatin overcoat.

Part of the coated film is then exposed through a step wedge and processed to a color positive in accordance with Reversal Color Process X described below, at about 24° C.

COLOR PROCESS X

	Min.
(1) Negative development	7-10
(2) Reversal flash exposure	
(3) Color development	7
(4) Clearing	5
(5) Silver bleaching	8
(6) Fixing	3
Wash and dry	

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NEGATIVE DEVELOPER (MQ)

Water, 9° F. (32° C.)	liters	1.0
Sodium hexametaphosphate	gm	2.0
N-methyl-p-aminophenol sulfate	gm	6.0
Sodium sulfite, desiccated	gm	50.0
Hydroquinone	gm	6.0
Sodium carbonate, monohydrate	gm	35.0
Potassium bromide	gm	2.0
Sodium thiocyanate	gm	1.5
6.5% solution of 6-nitrobenzimidazole nitrate	cc	12.0
0.1% solution of potassium iodide	cc	10.0

COLOR DEVELOPER

Water, 70° to 80° F. (21° to 27° C.)	liters	1.0
Benzyl alcohol	cc	6.0
Sodium hexametaphosphate	gm	2.0
Sodium sulfite, desiccated	gm	5.0
Trisodium phosphate	gm	40.0
Potassium bromide	gm	40.0
0.1% solution of potassium iodide	cc	6.5
Sodium hydroxide	gm	6.5
4-amino-N-(β-methanesulfonamidoethyl)-m-toluidinesulfate monohydrate	gm	11.33
Ethylenediamine sulfate	gm	7.8
Citrazinic acid (2,6-dihydroxyisonicotinic acid)	gm	1.5

CLEARING BATH

Water	liters	1.0
Sodium bisulfite	gm	10.0
Hydroquinone	gm	.5

SILVER BLEACHING SOLUTION

	Gm.
Sodium ferricyanide	60.0
Sodium hypophosphate·H ₂ O	17.6
Sodium bromide	15.0
Sodium hydroxide	3.5
Sodium thiocyanate	5.0
Water to 1 liter.	

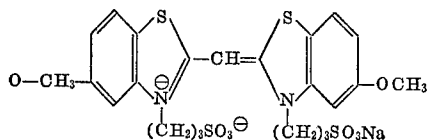
FIXING BATH

Water 80° F. (27° C.)	liters	1.0
Sodium thiosulfate	gm	95.6
Sodium bisulfite	gm	20.0

The results obtained are evaluated and reported in Table I below.

EXAMPLE II

A test film strip of camera speed and identified as (B), is prepared in the same manner as in Example I with the exception that the sensitizing dye utilized in the blue-sensitized bromiodide emulsion layer (layer 7) is an equimolar amount of a compound of the formula



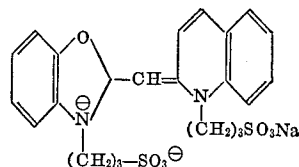
part of the film is exposed, processed, and evaluated as in Example I and reported in Table I.

EXAMPLE III

A test film strip of camera speed and identified as (C), is prepared in the same manner as in Example 1 with the exception that the sensitizing dye utilized in the blue-

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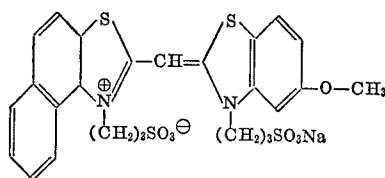
sensitized bromiodide emulsion layer (layer 7) is an equimolar amount of a compound of the formula



part of the film is exposed, processed and evaluated as in Example I and reported in Table I.

EXAMPLE IV

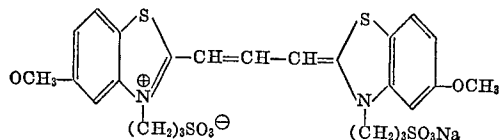
A test film strip of camera speed and identified as (D), is prepared as in Examples I and II with the exception that the blue-sensitizing dye of layer (7) is an equimolar amount of a compound of the formula



part of the film is then exposed, processed, and evaluated as in Example I and reported in Table I.

EXAMPLE V

A test film strip of camera speed and identified as (E), is prepared as in Examples I-IV with the exception that the blue sensitizer dye of layer (7) is outside of the present invention and consists of an equimolar amount of a compound of the formula



part of the film strip is then exposed, processed and evaluated as in Examples I-IV and reported in Table I.

TABLE I

Test film strip:	$\alpha_{\max}(\text{nm.})$
A	495
B	480
C	485
D	485
E	600

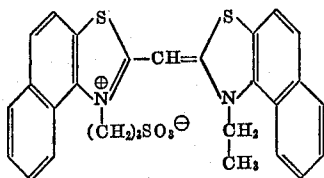
Test strips (A)-(D) of the present invention demonstrate good blue speed despite the use of a filter substantially cutting off those parts of the lower blue spectrum commonly associated with haze-scattering effects. Strip (E), utilizing a sensitizing dye in layer 7 outside of the present invention, on the other hand, exhibits a substantially lower blue speed for the magenta image.

EXAMPLE VI

A test film strip of camera speed and identified as (F), is prepared by coating a transparent cellulose acetate support layer with an antihalation and a subbing layer as in Examples I-III; applied to this combination

- (1) are the following layers;
- (2) a red-sensitive silver bromiodide gelatin emulsion layer having incorporated thereon the two cyan dye-forming couplers of Example 1 layer (3) in the same amount;
- (3) a green-sensitized silver bromiodide gelatin emulsion layer (6.3 mole percent iodide) coated at 240 mg. silver/ft.² and 440 mg. gelatin/ft.² into which is dispersed the magenta dye-forming coupler of Example I layer 7;

- (4) a gelatin interlayer;
- (5) a Carey-Lea filter layer;
- (6) a gelatin interlayer;
- (7) a blue-sensitized silver bromoiodide gelatin emulsion as in Example I layer (7) except that the dispersed coupler is the yellow dye-forming coupler used in Example I layer (3), and the incorporated sensitizing dye is a compound of the formula



utilized in the same molar amount as in Example I; and (8) a protective overcoat layer.

EXAMPLE VII

Camera speed films identified respectively as strips A (Example I) and F (Example VI) are separately exposed in the same model 35 mm. camera equipped with a Wratten 3 take-out filter and enclosed for underwater photography; the exposures being made vertically downward from just below the surface to record two divers carrying color plates, at pre-set depths varying from 5' to 100', in sea water under clear conditions, and at optimum camera settings; the films are then developed, evaluated, and the results recorded in Table II below.

TABLE II

Film strip	Depth (feet)	Comments
F-----	5	Excellent detail; color comparable to an above-surface shot at same distance.
	10	Do.
	25	Figures clear and distinct; good color differentiation with some loss in orange and red record compared with surface exposure.
	50	Figures distinguishable but not clear; washed-out color record with faint greens and grays observed.
	75	Figures very indistinct; no color record.
A-----	100	Figures not distinguishable; no color record; color plate not observable.
	5	Excellent detail; color comparable to above-surface shot at same distance.
	10	Do.
	25	Figures clear and distinct; no loss in color record compared with surface exposure.
	50	Figures clear and distinguishable; color retained in magenta and green.
	75	Figures distinguishable; a faint magenta and green record observable.
	100	Figures indistinguishable; no color; outline of color plate still observable.

No meaningful results are obtained using film strip (F) at a vertical distance beyond 50 feet, while strip (A) of the present invention recorded accurately and distinctly in the 50-75 ft. range, with some detail at 100 feet.

EXAMPLE VIII

Test film strips (A) and (F), as above described, are separately exposed underwater in a horizontal direction at a depth of 50 feet, using the same model equipment, subject matter and general conditions described in Example VII, and the exposed films developed, evaluated and results recorded in Table III.

TABLE III

Film strip	Depth (feet)	Distance (feet)	Comments
F-----	50	5	Excellent detail in every respect; a slight loss in red compared with surface photograph at same distance.
		10	Very good detail; observed loss in oranges and reds.
	50	25	Figures clear and distinguishable; substantial fade in all colors recorded.
		50	Figures indistinct; faint color record.
	50	75	Figures not distinguishable; no color record.
		100	Figures not distinguishable; no color record; no color plate observed.

TABLE III--Continued

Film Strip	Depth (feet)	Distance (feet)	Comments
A-----	50	5	Excellent detail in every respect; no color loss compared with surface photograph at same distance.
		10	Very good detail; no color loss compared with surface photograph at same distance.
	50	25	Figures clear and distinguishable; some color fade but blue and green record is very good; good color differentiation.
10	50	50	Figures distinct and clear; good color record in blue and green.
		75	Figures still distinguishable; faint color record.
	50	100	Figures not distinguishable; no color observed but color plate outline seen.
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EXAMPLE IX

A test film strip of camera speed, identified as (G) is prepared as in Example VI, except that layers 6-7 (i.e., a gelatin interlayer, and the blue-sensitized silver bromoiodide emulsion) are omitted.

EXAMPLE X

Three test film strips identified as (A), (F) and (G), as described in Examples I, VI and IX respectively, are loaded into three identical model aerial cameras equipped with No. 3 Wratten take-out filters and used to photograph a clear ocean bay having a gradient depth of 80-0 feet in the vicinity of Grand Cayman Island, West Indies, at a height of 10,000 feet, at the same camera settings. After developing, the three films are evaluated and the test results reported in Table IV.

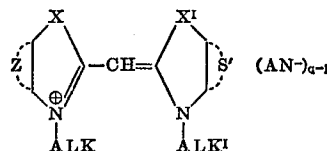
TABLE IV

Film strip	Estimated depth	Comments
(F)-----	0-10	Excellent detail.
	15-20	Do.
	25-35	Very good detail.
	50-80	Fair to poor detail; very faint color record in shallower depths; no color record at 70-80 feet.
(G)-----	0-10	Excellent detail.
	15-20	Good detail.
	25-35	Fair detail.
	50-80	Very poor or no detail; no color record.
(A)-----	0-10	Excellent detail.
	15-20	Do.
	25-35	Very good detail.
	50-80	Good detail; a faint color record observed at deepest point.

This invention has been described in detail with particular reference to a preferred embodiment 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. A color photographic element comprising a support layer having coated thereon two light-sensitive emulsion layers comprising
 - an inner green-sensitized silver halide emulsion layer responsive to light having a wavelength within about 525-590 nm.;
 - a blue-sensitized silver halide emulsion layer having a maximum light absorption wavelength within about 480-500 nm. and having substantially no light absorption above about 510 nm., sensitized with at least one compound having the formula



wherein

Z is defined as carbon and hydrogen atoms which, in combination with X, complete a benzothiazole radical, a benzoselenazole radical, a benzoxazole radical, a naphthothiazole radical or a naphthoselenazole radical;

X is defined as —O—, —S—, or —Se—;

Z' is defined as the carbon and hydrogen atoms which, in combination with X^I complete a quinoline radical when X and Z in combination define a benzoxazole radical, Z' being otherwise defined as the carbon and hydrogen atoms which in combination with X^I complete a benzothiazole radical, a benzoselenazole radical, a naphthothiazole radical or a naphthoselenazole radicals; and X^I is defined as —S—, —Se—, or the carbon and hydrogen atoms required to complete a quinoline radical;

ALK and ALK^I individually represent an alkyl group of 1-15 carbon atoms;

AN is an acid anion group;

q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is defined as a sulfoalkyl group or a carboxyalkyl group; plus

a light filter positioned between the green- and blue-sensitized emulsion layers, filtering light having a wavelength in the range of about 400-520 nm., the green- and blue-sensitized emulsion layers each containing at least one photographic coupler capable of forming a dye with oxidized aromatic primary amino color developing agents, the dyes found in the respective emulsion layers being different subtractive primary colors.

2. The photographic element of claim 1 where

X and Z are defined in combination to complete a benzoxazole radical; and

X^I and Z' are defined, in combination, to complete a 2-quinoline radical.

3. The photographic element of claim 1 wherein

X and Z are defined in combination to complete a 5- or 6-lower alkoxy-substituted benzothiazole, a 5- or 6-lower alkoxy-substituted benzoselenazole,

a naphtho [1,2-d] thiazole, a naphtho [2,1-d] thiazole or a naphtho [2,3-d] thiazole radical; and

X^I and Z' are defined as in X and Z.

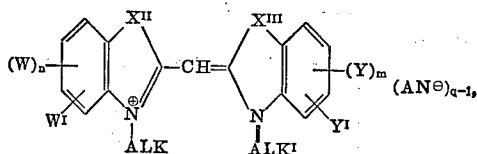
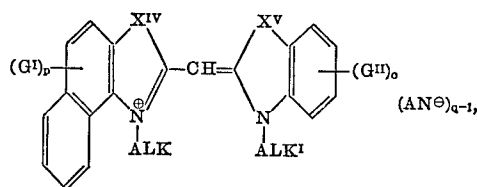
4. A photographic element comprising a support layer having coated thereon two light-sensitive emulsion layers comprising

an inner green-sensitized silver halide emulsion layer responsive to light having a wavelength within about 525-590 nm. and containing at least one cyan and one cyan and one yellow dye-producing coupler compound;

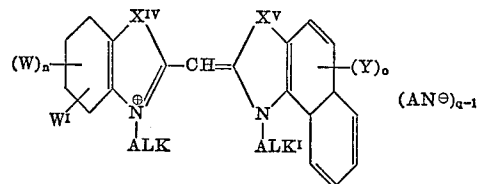
a blue-sensitized silver halide emulsion layer having a maximum light absorption wavelength within about 480-500 nm. with substantially no light absorption above about 510 nm., said blue-sensitized emulsion layer containing at least one magenta dye-forming coupler and at least one blue spectral sensitizer dye;

a filter layer positioned between the green- and blue-sensitized emulsion layers and filtering light having a wavelength in the range of about 400-520 nm.;

the sensitizer dye of the blue-sensitized emulsion layer having the formulae



or



wherein

W and Y are individually defined as a halo group, an alkoxy group, or an aryl group;

W^I, Y^I, G^I and G'^I are individually defined as hydrogen, a halo group or an alkyl group;

X^{II} is —O—, —S— or —Se—;

X^{III} is defined as the carbon and hydrogen atoms required to complete a quinoline radical when X^{II} is —O— and otherwise as —S— or —Se—;

X^{IV} and X^V are individually defined as —S— or —Se—;

m, n and o are integers of 0-3;

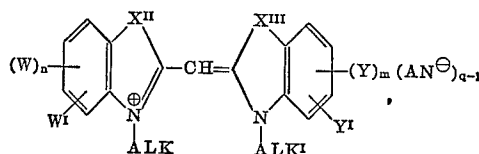
p is an integer of 0-1;

ALK and ALK^I individually represent an alkyl group of 1-15 carbon atoms;

AN is an acid anion group; and

q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is defined as a sulfoalkyl group or a carboxyalkyl group.

5. A photographic element of claim 4 wherein the blue spectral sensitizer dye is a compound having the formula



wherein

W and Y are individually defined as a halo group, an alkoxy group of 1-20 carbon atoms, a phenyl group, or a naphthyl group;

W^I and Y^I are individually defined as hydrogen, a halo group or and alkyl group of 1-20 carbon atoms;

X^{II} is —S—, —Se— or —O—;

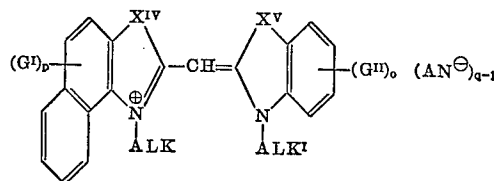
X^{III} is defined as the carbon and hydrogen atoms required to complete a quinoline radical when X^{II} is —O— and otherwise defined as —S— or —Se—;

n and m are integers of 0-2;

AN is an acid anion group;

ALK is a sulfoalkyl group or a carboxyalkyl group; ALK^I is a sodium or potassium sulfoalkyl group or a sodium or potassium carboxyalkyl group; and q is 1.

6. A photographic element of claim 4 wherein the blue spectral sensitizer dye is a compound of the formula

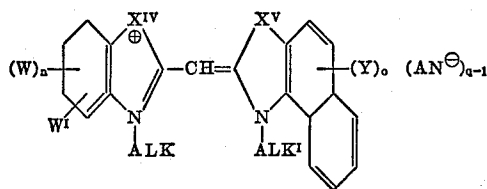


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wherein

G^I and G^{II} are individually defined as hydrogen, a halo group, or an alkyl group of 1-20 carbon atoms;
 X^{IV} and X^V are individually defined as $-S-$ or $-Se-$; 5
 o is 0-2;
 p is 0-1;
 ALK and ALK^I individually represent an alkyl group;
 AN is an acid anion; and
 q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is a sulfoalkyl group or a carboxyalkyl group.

7. A photographic element of claim 4 wherein the blue spectral sensitizer dye is a compound of the formula



wherein

W and Y are individually defined as a halo group, an alkoxy group, a phenyl group or a naphthyl group;
 W^I is a hydrogen atom, a halo group, or an alkyl group of 1-20 carbon atoms.
 X^{IV} and X^V are individually defined as $-S-$ or $-Se-$;
 n and o are individually defined as 0-2;
 ALK and ALK^I individually represent an alkyl group;
 AN is an acid anion; and
 q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is a sulfoalkyl group or a carboxyalkyl group.

8. A photographic element of claim 1 wherein the green-sensitized silver halide emulsion layer contains at least one phenolic or α -naphtholic cyan dye-forming coupler and at least one open-chained ketomethylene yellow dye-forming coupler compound and wherein the blue-sensitized emulsion layer contains at least one 5-pyrazolone magenta dye-forming coupler.

9. A photographic element of claim 4 wherein the green-sensitized silver halide emulsion layer contains 5-[α -(2,4-di-tert.-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol; 1-hydroxy-2-[Δ -(2,4-di-tert.-amylphenoxy)-N-butyl]-naphthamide; and α -pivalyl- α -(4-carboxyphenoxy)-2-chloro-5-[α -(3-N-pentadecylphenoxy)butyramido]-acetanilide as coupler components; and

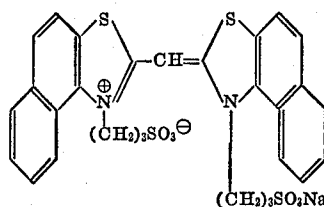
the blue-sensitized emulsion layer contains 1-(2,4,6-trichlorophenyl)-3-[3-[α -(3-pentadecylphenoxy)-butyramido]-benzamido]-5-pyrazolone as a magenta dye-forming coupler.

10. A color photographic element comprising a transparent film support layer;
 a green-sensitized silver halide gelatin emulsion containing 5-[α -(2,4-di-tert.-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol; 1-hydroxy-2-[Δ -(2,4-di-tert.-amylphenoxy)-N-butyl]-naphthamide; and α -pivalyl- α -(4-carboxyphenoxy)-2-chloro-5-[α -(3-N-pentadecylphenoxy)butyramido]-acetanilide as coupler components;

a dye-containing gelatin filter layer which absorbs light at about 400-520 nm; and

a blue-sensitized silver halide gelatin emulsion layer containing 1-(2,4,6-trichlorophenyl)-3-[3-[α -(3-pentadecylphenoxy)-butyramido]-benzamido]-5-pyrazolone as a magenta dye-forming coupler plus a blue spectral sensitizing dye of the formula

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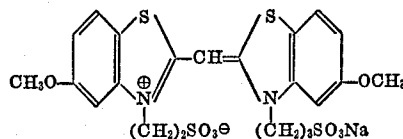
11. A color photographic element comprising a transparent film support layer;

a green-sensitized silver halide gelatin emulsion containing 5-[α -(2,4-di-tert.-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol; 1-hydroxy-2-[Δ -(2,4-di-tert.-amylphenoxy)-N-butyl]-naphthamide; and α -pivalyl- α -(4-carboxyphenoxy)-2-chloro-5-[α -(3-N-pentadecylphenoxy)butyramido]-acetanilide as coupler components;

a dye-containing gelatin filter layer which absorbs light at about 400-520 nm; and

emulsion layers each containing at least one photographic coupler capable of forming a dye with oxidized aromatic primary amino color developing agents, the dyes formed in the respective emulsion layers being different subtractive primary colors;

a blue-sensitized silver halide gelatin emulsion layer containing 1-(2,4,6-trichlorophenyl)-3-[3-[α -(3-pentadecylphenoxy)-butyramido]-benzamido]-5-pyrazolone as a magenta dye-forming coupler plus a blue spectral sensitizing dye of the formula

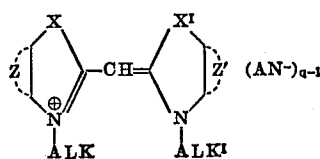


12. A color photographic element of claim 1 having incorporated therein external to said blue sensitized silver halide emulsion layer a filter layer containing one or more filter dyes which substantially absorb ultraviolet and visible blue light having wavelength up to about 480 nm.

13. The photographic element of claim 12 wherein the filter dyes are bis [1,3-diethylbarbituric acid (5)] methinoxonol or bis [3-phenyl-2-isoxazolin-5-one (4)] methinoxonol, pyridine salt.

14. A method for obtaining improved photographic records of water-submerged objects from above or below the surface comprising photographing said objects through a filter which absorbs at least about 80% of ultraviolet and blue light having a wavelength up to about 480 nm. with a camera utilizing, as a light-sensitive photographic element, an element comprising a support layer having coated thereon two light-sensitive emulsion layers comprising

an inner green-sensitized silver halide emulsion layer responsive to light having a wavelength within about 525-590 nm.; a blue-sensitized silver halide emulsion layer having a maximum light absorption wavelength within about 480-500 nm. and having substantially no light absorption with a wavelength above about 510 nm., and containing a blue spectral sensitizer dye having the formula



wherein

Z is defined as carbon and hydrogen atoms which, in combination with X , complete a benzothiazole radical, a benzoselenazole radical, a benzoxazole radical, a naphthothiazole radical or a naphthoselenazole radical;

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X is defined as —O—, —S—, or —Se—;

Z' is defined as the carbon and hydrogen atoms which, in combination with X^I complete a quinoline radical when X and Z in combination define a benzoxazole radical, Z' being otherwise defined in combination define a benzoxazole radical, Z' being otherwise defined as the carbon and hydrogen atoms which in combination with X^I complete a benzothiazole radical, a benzoselenazole radical, a naphthothiazole radical or a naphthoselenazole radical; and

X^I is defined as —S—, Se—, or the carbon and hydrogen atoms required to complete a quinoline radical;

ALK and ALK^I individually represent an alkyl of 1–15 carbon atoms;

AN is an acid anion group;

q represents an integer of 1–2 such that q is 1 when at least one of ALK or ALK^I is defined as a sulfoalkyl group or a carboxyalkyl group; plus

a light filter positioned between the green- and blue-sensitized emulsion layers and filtering light having a wavelength in the range of about 400–520 nm., the green- and blue-sensitized emulsion layers each containing at least one photographic coupler capable of forming a dye with oxidized aromatic primary amino color developing agents, the dyes found in the respective emulsion layers being different subtractive primary colors.

15. A method of claim 14 wherein

X and Z are defined in combination to complete a benzoxazole radical; and

X^I and Z' are defined, in combination, to complete a 2-quinoline radical.

16. A method of claim 14 wherein

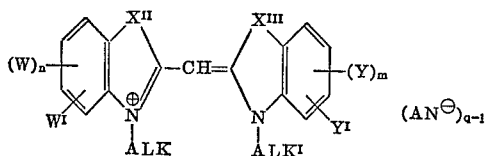
X and Z are defined in combination to complete a 5- or 6-lower alkoxy-substituted benzothiazole, a 5- or 6-lower alkoxy-substituted benzoselenazole, a naphtho [1,2-d]thiazole, a naphtho [2,1-d]thiazole or a naphtho [2,3-d]thiazole radical; and

X^I and Z' are defined as in X and Z.

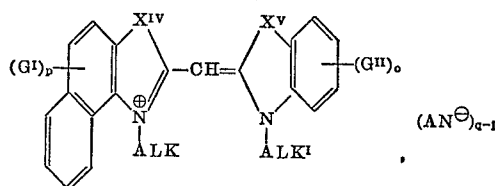
17. A method for obtaining improved photographic records of water-submerged objects from above or below the surface comprising

exposing said objects through a filter which absorbs at least about 80% of ultraviolet and blue light having a wavelength up to about 480 nm. with a camera utilizing, as a light-sensitive photographic element, an element comprising a support layer having coated thereon two light-sensitive emulsion layers comprising an inner-green-sensitized emulsion layer responsive to light having a wavelength within about 525–590 nm. and containing at least one cyan and one yellow dye-producing coupler compound; a blue-sensitized emulsion layer having a maximum light absorption wavelength within about 480–500 nm. and having substantially no light absorption with a wavelength above about 510 nm. and containing at least one magenta dye-forming coupler and at least one blue spectral sensitizer dye; a filter layer positioned between the green- and blue-sensitized emulsion layers and having light-absorption properties in the range of about 400–520 nm.;

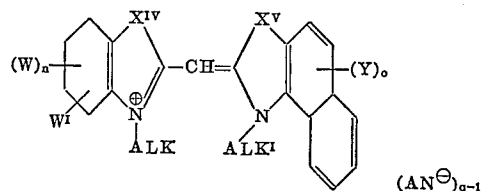
the sensitizer dye of the blue-sensitized emulsion layer having the formulae



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or



wherein

W and Y are individually defined as a halo group, an alkoxy group, or an aryl group;

W^I, Y^I, G^I and G^{II} are individually defined as hydrogen, a halo group or an alkyl group;

X^{II} is —O—, —S— or —Se—;

X^{III} is defined as the carbon and hydrogen atoms required to complete a quinoline radical when X^{II} is —O— and otherwise as —S— and —Se—;

X^{IV} and X^V are individually defined as —S— or —Se—; m, n and o are integers of 0–3;

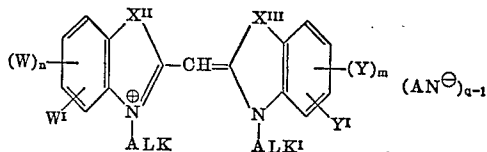
p is an integer of 0–1;

ALK and ALK^I individually represent an alkyl group of 1–15 carbon atoms;

AN is an acid group; and

q represents an integer of 1–2 such that q is 1 when at least one of ALK or ALK^I is defined as a sulfoalkyl group or a carboxyalkyl group.

18. A method of claim 17 wherein the blue spectral sensitizer dye is a compound of the formula



wherein

W and Y are individually defined as a halo group, an alkoxy group of 1–20 carbon atoms, a phenyl group, or a naphthyl group;

W^I and Y^I are individually defined as hydrogen, a halo group or an alkyl group of 1–20 carbon atoms;

X^{II} is —S—, —Se— or —O—;

X^{III} is defined as the carbon and hydrogen atoms required to complete a quinoline radical when X^{II} is —O— and otherwise defined as —S— or —Se—;

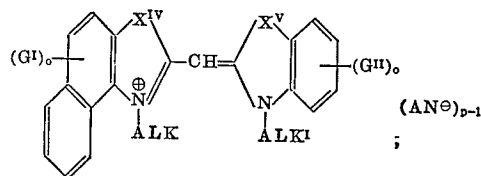
n and m are integers of 0–2;

AN is an acid anion group;

ALK is a sulfoalkyl group or a carboxyalkyl group;

ALK^I is a sodium or potassium sulfoalkyl group or a sodium or potassium carboxyalkyl group; and q is 1.

19. A method of claim 17 wherein the blue spectral sensitizer dye is a compound of the formula



wherein

G^I and G^{II} are individually defined as hydrogen, a halo group, or an alkyl group of 1–20 carbon atoms;

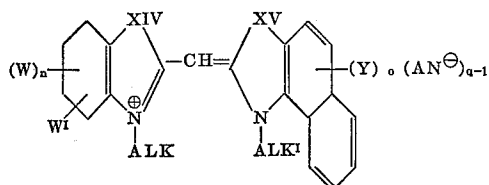
19

X^{IV} and X^V are individually defined as $-S-$ or $-Se-$;
 o is 0-2;
 p is 0-1;

ALK and ALK^I individually represent an alkyl group;
 AN is an acid anion; and

q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is a sulfoalkyl group or a carboxyalkyl group.

20. A method of claim 17 wherein the blue spectral sensitizer dye is a compound of the formula



wherein

W and Y are individually defined as a halo group, an alkoxy group, a phenyl group or a naphthyl group;

Wt is a hydrogen atom, a halo group, or an alkyl group of 1-20 carbon atoms;

X^{IV} and X^V are individually defined as $-S-$ or $-Se-$;
 n and o are individually defined as 0-2;

ALK and ALK^I individually represent an alkyl group;
 AN is an acid anion; and

q represents an integer of 1-2 such that q is 1 when at least one of ALK or ALK^I is a sulfoalkyl group or a carboxyalkyl group.

21. A method of claim 17 wherein the green-sensitized silver halide emulsion layer contains at least one phenolic or α -naphtholic cyan dye-forming coupler and at least one open-chained ketomethylene yellow dye-forming coupler compound and wherein the blue-sensitized emulsion layer contains at least one 5-pyrazolone magenta dye-forming coupler.

22. A method of claim 17 wherein the

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green-sensitized silver halide emulsion layer contains 5 - [α - (2,4 - di-tert.-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol; 1 - hydroxy - 2 - [Δ -(2,4 - di-tert.-amylphenoxy)-N-butyl]-naphthamide; and α -pivalyl- α -(4 - carboxyphenoxy)-2-chloro-5-[α -(3 - N - pentadecylphenoxy)butyramido]-acetanilide as coupler components; and

the blue-sensitized emulsion layer contains 1-(2,4,6-trichlorophenyl)-3-[3 - { α - (3-pentadecylphenoxy)-butyramido}-benzamido]-5-pyrazolone as a magenta dye-forming coupler.

23. A method of claim 17 wherein the green-sensitized silver halide emulsion layer contains 5 - [α - 2,4 - di-tert.-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenol; 1 - hydroxy - 2 - [Δ -(2,4 - di-tert.-amylphenoxy)-N-butyl]-naphthamide; and α -pivalyl- α -(4 - carboxyphenoxy) - 2 - chloro-5-[α -(3 - N - pentadecylphenoxy)butyramido]-acetanilide as coupler components; and

the blue-sensitized emulsion layer contains 1-(2,4,6-trichlorophenyl) - 3 - [3-{ α -(3-pentadecylphenoxy)-butyramido}-benzamido]-5-pyrazolone as a magenta dye-forming coupler.

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NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

40 96-132; 352-45

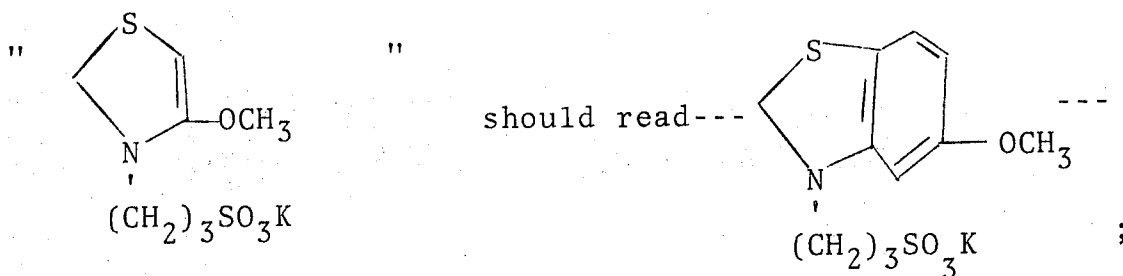
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,752,670 Dated August 14, 1973

Inventor(s) Daniel G. Needler and James L. Graham

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 58, in that part of Formula (9)



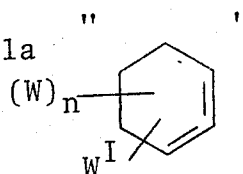
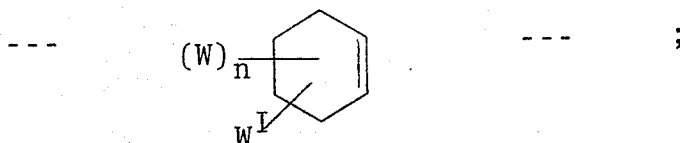
Column 9, line 21, "40.0" should read --- 0.25 ---;

Column 9, line 22, "6.5" should read --- 10.0 ---;

Column 12, line 72, that part of the formula "S' " should read --- Z' ---;

Column 13, line 16, "radicals" should read ---radical---;

Column 15, line 22, that part of the formula



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 2

Patent No. 3,752,670 Dated August 14, 1973
Inventor(s) Daniel G. Needler and James L. Graham

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 16, line 16, "naphthalamide" should read
---naphthamide---;

Column 18, line 67, in that part of the formula
"(G^I)_o" should read --- (G^I)_p ---.

Signed and sealed this 23rd day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

G. MARSHALL DANN
Commissioner of Patents