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

(11) EP 1 160 620 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.12.2001 Bulletin 2001/49

(51) Int Cl.^{7}: **G03C 1/34**

(21) Application number: **01201707.5**

(22) Date of filing: **10.05.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **22.05.2000 US 575754**

(71) Applicant: **EASTMAN KODAK COMPANY**
Rochester, New York 14650 (US)

(72) Inventors:
- **Lushington, Kenneth James,**
  Eastman Kodak Company
  Rochester, NY 14650-2201 (US)
- **Singer, Stephen Paul, Eastman Kodak Company**
  Rochester, NY 14650-2201 (US)

(74) Representative:
Nunney, Ronald Frederick Adolphe et al
Kodak Limited,
Patents, W92-3A,
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)

(54) Photographic element containing antifoggant

(57) Disclosed is a photographic element comprising a layer containing a silver halide emulsion chemically or spectrally sensitized or both in the presence a heterocycle compound with a minimum of three heteroatoms that does not react with oxidized developer and has a ClogP greater or equal to 6.2. The invention provides decreased fog while maintaining light sensitivity.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] Photographic Sensitivity, Theory and Mechanisms, Oxford University Press, NY, 1995, Section 6.5. In particular, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (ClogP (as hereinafter defined) = -0.27) is widely used in photographic films and in the preparation of light sensitive silver halide emulsions.

[0002] Copending application U.S. 09/221,359 discloses the use of compounds with three or more heteroatoms with a ClogP of greater than 6.2 as addenda to increase overall light sensitivity. However, these materials are not added directly to the silver halide emulsion and require levels equal to or greater than 1 mmol of compound per mole of silver present in the same layer and do not significantly inhibit fog when used as described within.

[0003] US 4,400,463 discloses the use of 6-aminopurine (also known as adenine; ClogP = -0.34 and other aminoazaindenes as growth modifiers in the preparation of silver halide emulsions. E. Klein and E. Moisar, Berichte der Bungesellschaft, 67 (4), 349-355, 1963, report an inhibiting effect upon the grain growth of silver chloride when purine bases, such as adenine, are added at various stages of emulsion precipitation. U.S. 3,519,426 discloses the preparation of silver chloride emulsions of increased covering power by precipitating in the presence of an azaindene, such as a tetraazaindene, pentaazaindene, or adenine. Specific aminoazaindenes known to be useful in photographic emulsions as stabilizers are also illustrated by U.S. 2,444,605, U.S. 2,743,181 and 2,772,164. US 5,230,995 describes the use of various heterocycles, including tetraazaindenes, mercaptotetrazoles and mercaptothiadiazoles, as addenda used in the manufacture of silver halide emulsions substantially free of iodide. US 5,116,723 describes the use of a wide variety of heterocycles in combination with certain sulfur containing compounds that can be added during the preparation of silver halide emulsions of not less than 90 mole % chloride. In all of these references, the heterocycles are water soluble and have a ClogP of less than 6.2.

[0004] US 5,260,183 describes photographic elements which use 1,3,3a,7-and 1,2,3a,7-tetraazaindenes with silver halide emulsions of at least 80 mole % chloride, which additionally contain thiocyanate and are sensitized with certain cyanine dyes, in order to promote J-band aggregation of the cyanine dyes. Such heterocycles are described as being added at any time prior to the coating of the elements (Column 25, lines 28-35). Of the 35 heterocyclic examples shown, only one (II-17; ClogP = 8.19) has a ClogP greater than 6.2.

[0005] The antifoggant materials described above generally have the deficiency that while they control fog in a silver halide emulsion, they also cause some decrease in the overall sensitivity to light. In addition, such fully or partially water soluble materials like the above can diffuse to adjacent imaging layers where they can also decrease light sensitivity.

[0006] A problem to be solved is to provide color photographic elements that exhibit low fog while maintaining light sensitivity.

[0007] The invention provides a photographic element comprising a layer containing a silver halide emulsion chemically or spectrally sensitized or both in the presence a heterocycle compound with a minimum of three heteroatoms that does not react with oxidized developer and has a ClogP greater or equal to 6.2.

[0008] In certain embodiments of the invention, the silver halide emulsion comprises an iodobromide emulsion, is sensitized to green light, comprises a particular grain size, and is present in a desirable proportion to silver. In other embodiments of the invention, the compound is a particular kind of heterocycle with a minimum of three heteroatoms including a tetraazaindene, a benzotriazole, a triazole, a tetrazole, a thiadiazole or a oxadiazole and is dispersed in a hydrophobic organic solvent.

[0009] The invention provides photographic elements and emulsions that exhibit low fog while maintaining light sensitivity and methods for preparing and processing such elements.

[0010] The invention is as generally described above. The element may be either a color photographic element or a black and white element.

[0011] Black and white elements are well known and discussed in the publications cited hereinafter. Such elements rely on the reduced silver for image formation. In one embodiment of the invention, an emulsion in such a black and white element contains the heterocyclic compound useful in the invention.

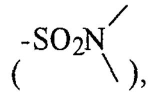
[0012] In another embodiment, the present invention relates to a color photographic element designed to reproduce images in color comprising at least one red sensitive silver halide emulsion layer with at least one non-diffusing cyan coupler, at least one green sensitive silver halide emulsion layer with at least one non-diffusing magenta coupler and at least one blue sensitive silver halide emulsion layer with at least one non-diffusing yellow coupler, characterized in that, for at least one light sensitive silver halide emulsion layer, the silver halide emulsion contains a heterocycle compound with a minimum of three heteroatoms that does not react with oxidized developer and has a ClogP greater or equal to 6.2

[0013] The term " heteroatom" as used herein encompasses any atom other than carbon that is an integral member of the heterocyclic ring system. It does not encompass atoms bonded to ring member atoms nor atoms that are located externally to the ring system that form part of a substituent of the ring system. Examples of suitable heteroatoms include nitrogen, sulfur, phosphorous and oxygen.

[0014] The compounds useful in the invention, or "antifogging compounds", have a minimum hydrophobicity (as measured by ClogP) which allows them to minimize fog without causing a loss in overall sensitivity to light. Among the classes of compounds that contain a minimum of three heteroatoms that can be included in the invention when appropriately substituted to increase hydrophobicity are: triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, mercaptotetrazoles, selenotetrazoles, mercaptothiadiazoles, mercaptotriazoles, mercaptooxadiazoles, telleurotetrazoles, benzisodiazoles, thioureas, purines and other polyazaindenes. The optimum minimum ClogP for fog improvement may vary somewhat for each class of compound useful in this invention.

[0015] One preferred class of heterocycles useful in the invention is polycyclic nitrogen heterocycles, such as those that contain systems comprising at least two fused rings composed only of carbon and at least three nitrogen atoms. Specific examples of preferred polycyclic nitrogen heterocycles with at least three nitrogen atoms as part of the ring system are benzotriazoles and tetraazaindenes (including purines). Another preferred class of heterocycles useful in the invention are monocyclic heterocycles comprising carbon and at least two nitrogen atoms with at most only one ring sulfur or ring oxygen atom. Specific classes of these preferred heterocycles are triazoles, oxadiazoles, thiadiazoles and tetrazoles.

[0016] The substituents located directly on the heterocycles useful in the invention can be hydrogen or any group chosen such that together the entire compound meets the overall ClogP requirement. These substituents may be, for example, alkyl, aryl, alkoxy or aryloxy, alkylthio or arylthio, sulfoxyl, sulfonyl, sulfamoyl



$$\left(-SO_2N\!\!\begin{array}{l}/\\ \backslash\end{array}\right),$$

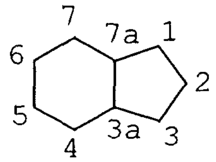
halo such as fluoro, chloro, bromo or iodo, cyano, thiol, hydroxy, nitro, -O-CO-, -O-SO_2-, a heterocyclic group such as furanyl or morpholino, a carbonyl group such as keto, carboxylic acid (-CO_2H), carboxylate ester (-CO_2-) or carbamoyl

$$\left(-CON\!\!\begin{array}{l}/\\ \backslash\end{array}\right)$$

or an amino group such as a primary, secondary or tertiary substituted nitrogen, carbonamido (>NCO-) or sulfonamido (>NSO_2-). A substituent may also connect two or more independent nitrogen heterocycle nuclei together so long as the entire molecule still meets the ClogP limitations. In addition, the substituent may further contain a group that can be incorporated into a polymeric backbone so long as the monomeric species meets the ClogP limitations. It should be noted wherever it is possible to write alternative tautomeric structures of the heterocyclic nucleus, these are considered to be chemically equivalent and are part of the invention.

[0017] More preferred forms of the polycyclic nitrogen heterocycles useful in the invention contain a 6/6 or 6/5 two-ring bicyclic nucleus in which the two rings contain at least 4 nitrogen atoms over both ring systems so long as no three nitrogen atoms are consecutive, that is, directly connected to each other, unless one of the three consecutive nitrogens occupies a bridgehead position or all three nitrogens are located in the same six membered ring. Any particular nitrogen atom may be part of only one ring or be located in a bridgehead position. A bridgehead position is where an atom forms part of more than one ring. In addition, it is possible that other ring systems may be annulated to these heterocyclic ring systems or even be located between these rings so long as two rings (at least one of which must be a six membered ring) contain, between them, at least 4 nitrogen atoms and do not contain 3 nitrogen atoms directly connected to each other unless one of the three nitrogens occupies a bridgehead position or all three nitrogens are located in the same six membered ring. The additional rings may or may not contain additional nitrogen atoms or other heteroatoms such as sulfur or oxygen. None of the rings that comprise the heterocyclic nucleus are isolated or joined only by a single bond. It is preferred that the heterocyclic nucleus be aromatic or pseudo-aromatic. Another preferred form of polycyclic nitrogen heterocycle is benzotriazole, which contains only 3 nitrogen atoms, that are connected to each other and none of which occupies a bridgehead position.

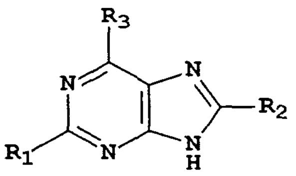
[0018] A particularly preferred form of the heterocycle useful in the invention is a 6/5 bicyclic aromatic nitrogen heterocycle that contains at least 4 nitrogen atoms as part of the ring system and does not contain 3 nitrogen atoms directly connected to each other unless one of the three nitrogen atoms occupies a bridgehead position or all three nitrogen atoms are located in the same six membered ring and is substituted so that the overall ClogP for the compound is at least 6.2. It is preferred that the ClogP should be at least 6.8 or suitably at least 7.2. It is also preferred that the ClogP be equal to or less than 13.0, conveniently less than 11.5. Some examples of the 6/5 bicyclic heterocycle compounds useful in the invention are the following tetraazaindenes and pentaazaindenes (numbered according to the structure below): 1,3,4,6 and 1,3,5,7 (both also known as purines); 1,3,5,6; 1,2,3a,4; 1,2,3a,5; 1,2,3a,6; 1,2,3a,7; 1,3,3a, 7; 1,2,4,6; 1,2,4,7; 1,2,5,6 and 1,2,5,7. These compounds may also be described as derivatives of imidazo, pyrazolo- or triazolo-pyrimidines, pyridazines or pyrazines. Some examples of pentaazaindenes are 1,2,3a,4,7; 1,2,3a,5,7 and 1,3,3a,5,7. An example of a hexaazaindene would be 1,2,3a,4,6,7.



The more preferred examples are in which the 6/5 bicyclic nitrogen heterocycle are 1,3,4,6; 1,2,5,7; 1,2,4,6; 1,2,3a,7 or 1,3,3a,7-tetraazaindene derivatives.

[0019] For these types of polycyclic nitrogen heterocycles, ionizable substituents, such as hydroxy (-OH), thiol (-SH) or non-tertiary amino groups (-H_2 or -NH-) are attached to a ring atom such that conjugation to a ring nitrogen can occur to provide tautomeric forms of the heterocycle. It is preferred to have none of this kind of substituent, unless there is a bridgehead nitrogen in which case it is preferred to have at most only one hydroxy or thiol group, to maintain the desired degree of silver interaction.

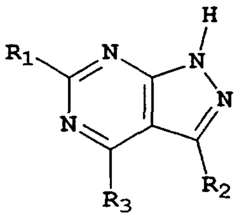
[0020] The most preferred examples of a purine derivative are according to Formula I:



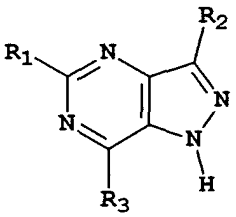
I

wherein R_1 and R_2 are each independently hydrogen or an alkyl, aryl, alkoxy or aryloxy, alkylthio or arylthio, sulfoxyl, sulfonyl, sulfamoyl, halo such as fluoro, chloro, bromo, and iodo, cyano, nitro, -O-CO-, -O-SO_2-, a heterocyclic group, a carbonyl group such as keto, carboxylic acid, carboxylate ester or carbamoyl or an amino group such as a primary, secondary or tertiary substituted nitrogen, carbonamido or sulfonamido. R_3 is an alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, sulfonyl, sulfoxyl, secondary or tertiary amino group, carbonamido group or a sulfonamido group all of which may be substituted as provided hereinafter. Compounds in which R_3 is an alkoxy or alkylthio group are especially preferred. The overall ClogP should be at least 6.2, or more preferably, at least 6.8 or most preferably, at least 7.2 with a maximum ClogP equal to or less than 13.0.

[0021] The most preferred examples of a 1,2,5,7-tetraazaindene derivative are according to Formula IIa or a 1,2,4,6-tetraazaindene derivative are according to Formula IIb:



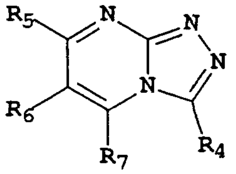
IIa



IIb

wherein R_1, R_2 and R_3 are each defined above. Compounds in which R_3 is an alkoxy or alkylthio group are especially preferred. The overall ClogP should be at least 6.2, or more preferably, at least 6.8 or most preferably, at least 7.2 with a maximum ClogP equal to or less than 13.0.

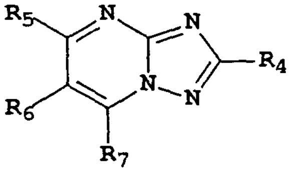
[0022] The most preferred examples of a 1,2,3a,7-tetraazaindene derivative are according to Formula III:



III

wherein R_4, R_5, R_6 and R_7 are each as defined for R_1 and R_2 but also including thiol or hydroxy groups. Especially preferred are compounds where R_7 is a hydroxy group, R_5 is an alkyl group and R_4 is the same as defined for R_3 with alkyl, aryl, alkoxy, arylthio, or alkylthio groups being particularly beneficial. The overall ClogP should be at least 6.2, or more preferably, at least 6.8 or most preferably, at least 7.2 with a maximum ClogP equal to or less than 13.0.

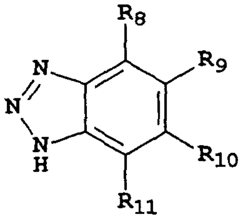
[0023] The most preferred examples of a 1,3,3a,7-tetraazaindene derivative are according to Formula IV:



IV

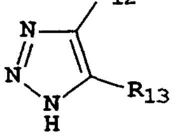
wherein R_4, R_5, R_6 and R_7 are the same as for Formula III. Especially preferred are compounds where R_7 is a hydroxy group, R_5 is an alkyl group and R_4 is the same as defined for R_3 with alkoxy or alkylthio groups being particularly beneficial. The overall ClogP should be at least 6.2, or more preferably, at least 6.8 or most preferably, at least 7.2 with a maximum ClogP equal to or less than 13.0.

[0024] Another preferred form of the heterocycle useful in the invention is a benzotriazole in which the overall ClogP for the compound is at least 7.8, or more preferably at least 8.2 or most preferably at least 9.0. It is also preferred that the ClogP be equal to or less than 13.0. The more preferred examples of a benzotriazole are according to Formula V wherein R_8, R_9, R_{10} and R_{11} are each individually defined as for R_1 and R_2 above. The most preferred examples of a benzotriazole derivative are where R_8 and R_{11} are hydrogen and where R_9 is a carboxylate ester, a carbamoyl group, a carbonamido group, a sulfonamido group or an alkoxy or aryloxy group.

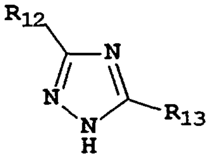


V

[0025] Another preferred form of the nitrogen heterocycle useful in the invention is a triazole in which the overall ClogP for the compound is at least 8.75, or more preferably at least 9.0 or most preferably at least 9.25 and equal t or less than 13.0. The more preferred examples of a triazole are 1,2,3-triazoles according to Formula VI and 1,2,4-triazoles according to Formula VII wherein R_{12} and R_{13} are each individually defined as for R_1 and R_2 above. The most preferred examples of triazoles are where R_{12} is hydrogen, alkyl or aryl and R_{13} is an alkylthio or arylthio, carboxylate ester or substituted alkyl group.

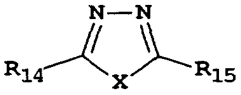


VI



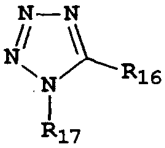
VII

[0026] Another preferred form of the nitrogen heterocycle useful in the invention is a diazole in which the overall ClogP for the compound is at least 7.6, or more preferably at least 7.9 or most preferably at least 8.2 and equal to or less than 11.5. The more preferred examples of a diazole are according to Formula VIII wherein X is oxygen or sulfur and R_{14} and R_{15} are each individually defined as for R_1 and R_2 but also including a thiol group. The most preferred examples of an oxadiazole or a thiadiazole are where R_{14} is a thiol group and R_{15} is an alkyl, aryl, alkylthio or arylthio or amino group.



VIII

[0027] Another preferred form of the nitrogen heterocycle useful in the invention is a tetrazole. The more preferred examples of a tetrazole are according to Formula IX wherein R_{16} is as defined for R_1 including a thiol (-SH) group (when R_{16} is a thiol group, such compounds are known as mercaptotetrazoles) and R_{17} is as defined as R_1. The most preferred examples of a tetrazole are when R_{16} is a thiol group and R_{17} is an alkyl, aryl or heterocyclic group; or when R_{17} is hydrogen and R_{16} is an alkyl, aryl, amino, alkoxy or aryloxy, heterocyclic or alkylthio or arylthio group. When R_{16} is a thiol group, then the ClogP for the compound should be at least 7.0 or more preferably at least 7.4 or most preferably at least 7.8 and preferably the ClogP should be equal or less than 13.0. When R_{16} is not a thiol group, then the ClogP for the compound should be at least 6.5 or more preferably at least 7.0 or most preferably at least 7.5 and should be less than or equal to 10.5.



IX

[0028] The compounds useful in the invention are not couplers and do not react with oxidized developer (Dox) to generate dyes or any other product. It is desired that the compounds useful in the invention do not undergo any significant amounts (less than 5-10%) of chemical or redox reaction directly with oxidized developer. They are colorless. They are stable to other components of the processing solutions and do not contain substituents that undergo substantial amounts of chemical reaction in any of the processing solutions. For example, the inventive materials do not contain hydrazino or hydroquinone groups that may cross-oxidize during silver development nor are they covalently linked to any other kind of photographic useful group (PUG). However, the inventive materials may contain, for example, ester substituents that are not substantially hydrolyzed (less than 5-10%) during the development process. The compounds useful in the invention are added to the emulsion located in the film element as described and are not added to the processing solutions.

[0029] An important feature of the compounds useful in the invention is their hydrophobicity which is related to their octanol/water partition coefficient (logP). In order to maximize the photographic effect, the partitioning into water cannot be so low that the material is unable to reach the surface of the emulsion grains. It has also been found that the partitioning into water cannot be too high. Because it can be difficult to measure logP values above 3, a model can be used to compute an estimate of logP, called ClogP that defines the limits of the invention. The model used is MEDCHEM Version 3.54, which is a software program produced by the Medicinal Chemistry Project at Pomona College in California.

[0030] One way to enter a structure into the MEDCHEM program in order to calculate a ClogP is through a SMILES string. The way to enter the SMILES string for a nitrogen compound is to enter all non-hydrogen atoms as capitals and let the MEDCHEM program determine the appropriate aromaticity. An example is shown for compound A below: CCCCCCCCCCCCCCCOC1=C2N=CNC2=NC=N1. This entry gives the value 6.91. When the entry is in this form, the heterocyclic N-H will be drawn in the structure by the MEDCHEM program. If the entry is not in this form, the MEDCHEM program will not display the heterocyclic N-H group and the resulting ClogP value is incorrect. Structures such as A and AJ can be drawn in multiple tautomeric forms, for example, hydrogens on different ring atoms, enol or keto tautomeric forms (or thiol or thione forms for sulfur compounds). If ClogP values can be calculated for more than one tautomeric form of a single compound and at least one of those values is within the specified range for that class, then the compound is within the scope of the invention. Some tautomers may not compute in MEDCHEM 3.54, because there is a fragment in the molecule that is missing in the MEDCHEM database. In such a case, logP of the nucleus of the molecule (with appropriate aromatic or aliphatic substituents) must be experimentally measured and the missing fragment value must be entered into the algorithm manager of MEDCHEM as instructed by the manual.

[0031] For the purposes of this invention, the ClogP refers to neutral molecules, even if they would be ionized or protonated (either fully or in part) at the processing pH or at the ambient pH of the photographic film. Thus, in practice, it is highly desirable that the substituents of the compound useful in the invention do not contain additional very low pK_a (<7) groups such as sulfonic or carboxylic acids nor very basic groups (pKa of conjugate acid < 10) such as a tertiary amino group (unless such an amino group is attached to a heterocylic ring such that it is conjugated to a nitrogen atom, in which case its basicity is greatly reduced) since they require an increase in the size and amount in the rest of the hydrophobic substituents in order to meet the overall ClogP requirements.

[0032] There is a specific range of ClogP for each class of compounds, depending on its particular nature, which should not be exceeded. For most examples, it is preferred that the ClogP not exceed 13.0 or more preferably for some types of compounds, not to exceed 11.5. In order to prevent loss in light sensitivity, the ClogP should not be lower than 6.2 and it is preferred that the ClogP of the compound be at least 6.8 or greater or even 7.2 or greater.

[0033] One of the most important and novel characteristics of the compounds of this invention is the finely tuned balance between their hydrophobic and hydrophilic nature. The hydrophobic/hydrophilic nature of a compound can be estimated by calculation of its partition coefficient between octanol and water (ClogP) using the MEDCHEM program, and this has been used herein to define the range of values of ClogP for each class of compound within which they exhibit the desired effect. The terms 'ballast' or 'ballasted' as generally applied in the photographic art are often applied only loosely and without quantification to imply a restriction of movement. The activity of the inventive compounds is therefore best defined in terms of their calculated ClogP values.

[0034] For each compound useful in the invention, there is an optimum laydown which should not be exceeded to order to minimize any loss in light sensitivity. Suitably, there is present sufficient laydown to achieve an improvement in fog of at least 0.001, and desirably at least 0.005 and even 0.010 density units or more. In general, the ratio of compound to silver is suitably less than 1.0 mmole of compound per mole of silver halide. It is preferred that the ratio of compound to silver is less than 0.10 mmole of compound per mol of silver halide and, more preferably, less than 0.05 mmole of compound per mole of silver halide.

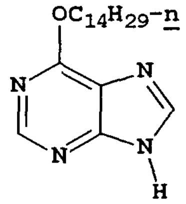
[0035] For the purposes of the invention, it is critical that the antifogging compounds are added, preferably as a dispersion in a hydrophobic organic solvent, directly to the silver halide emulsion prior to coating. Typically, silver halide emulsions are precipitated and washed (for example, as described in Chapter 3 of The Theory of the Photographic Process, 4th Edition, T.H. James, Ed., Macmillan Publishing Co, NY, 1977 or in US 4,400,463), treated with various types of chemicals to modify the surface and electronic properties ("chemical sensitization" as described, for example, in Chapter 5, *ibid*), as well as treated with sensitizing dyes and other types of surface active materials ("spectral sensitization" or "dye sensitization" as described, for example, in Chapter 9, *ibid*). The chemical and dye sensitization steps may be in any order or can be combined into a single step. It is also a common practice to use a heat digest or temperature increase of at least 5°C after the addition to improve the efficiency of the chemical or dye sensitization step; for example, see US 4,439,520, US 5,338,655 and references cited therein. At a subsequent time, the silver halide is added to other components of the layer (for example, couplers) and the mixture coated to make the final product. In general, it is known to add antifoggants at any step in this sequence. It is preferred that the compound useful in the invention be added after the precipitation and formation of the silver halide crystals but before the emulsion is prepared for incorporation into the final photographic element. It is most preferred that the heterocyclic compound be added prior to or concurrent with either the chemical sensitization of the silver halide crystals or the dye sensitization step. It is also most preferred that the compound be added prior to any heat digest of 5°C or more associated with the sensitization process.

[0036] The "emulsion" is distinguished from the "emulsion layer". At some time after emulsion preparation, the emulsion is combined with other components such as hydrophobic dispersions of couplers and/or other components and the mixture is then promptly coated to form an "emulsion layer" of the final product.

[0037] The following are examples of compounds, along with the corresponding ClogP values, that are useful in this invention:

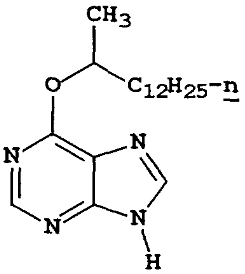
A:

(6.91)



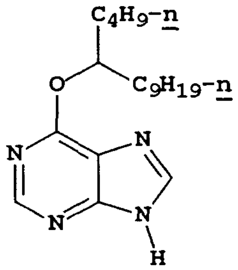
B:

(6.69)



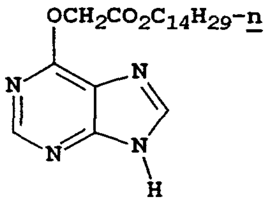
C:

(6.69)



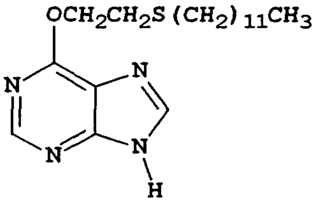
D:

(6.50)



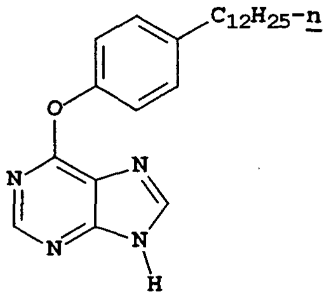
E:

(6.37)



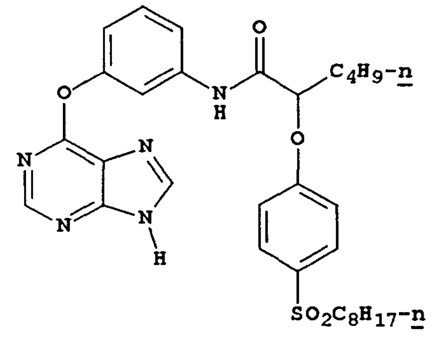
F:

(8.53)



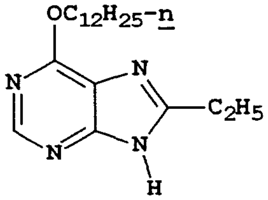
G:

(7.21)



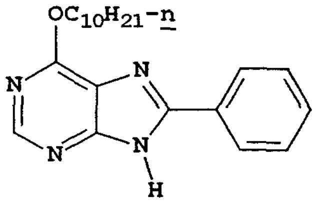
H:

(6.65)



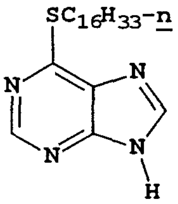
I:

(6.92)



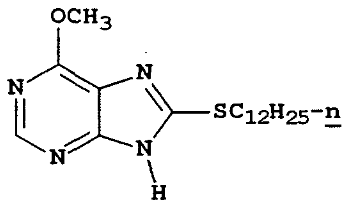
J:

(8.32)



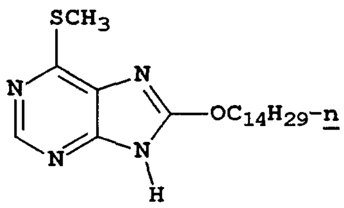
K:

(6.76)



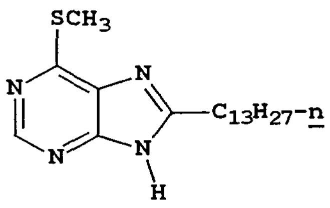
L:

(7.78)



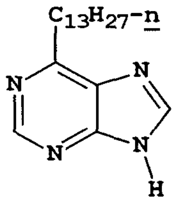
M:

(7.00)



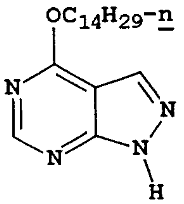
N:

(6.27)



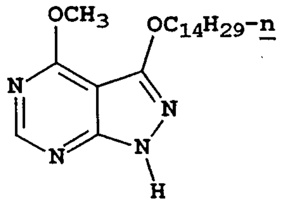
O:

(7.19)



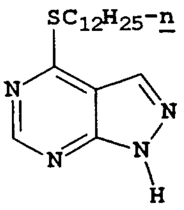
P:

(7.47)



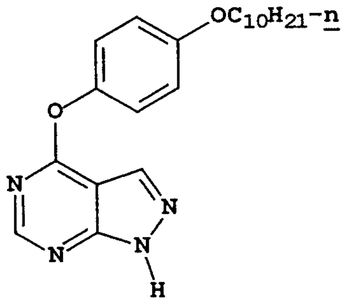
Q:

(6.49)



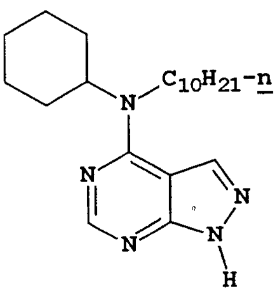
R:

(7.27)



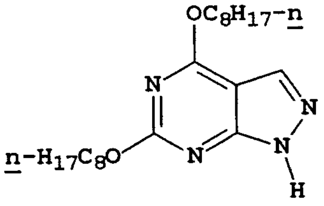
S:

(7.09)



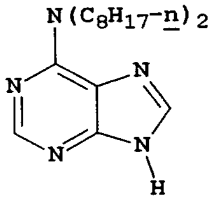
T:

(8.30)



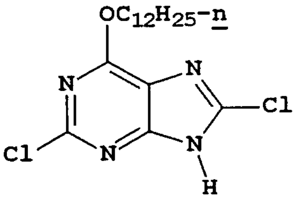
U:

(7.45)



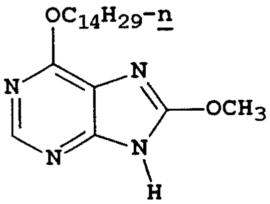
V:

(7.33)



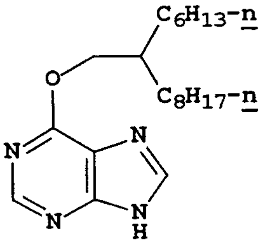
W:

(7.43)



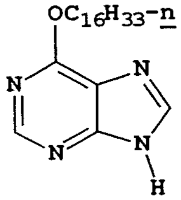
X:

(7.84)



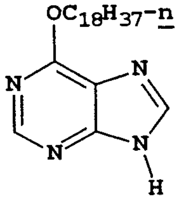
Y:

(7.97)



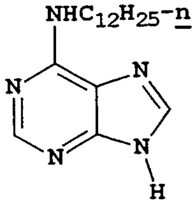
Z:

(9.03)



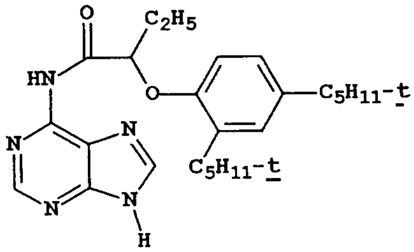
AA:

(6.21)



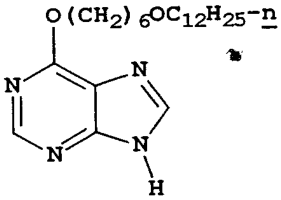
AB:

(6.98)



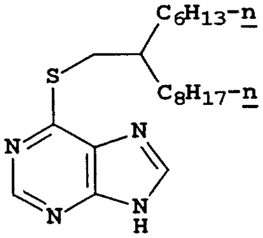
AC:

(7.09)



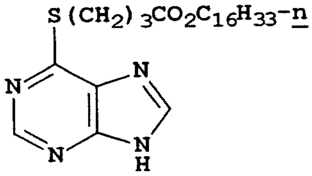
AD:

(8.19)



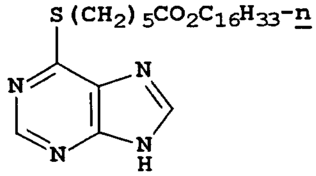
AE:

(8.30)

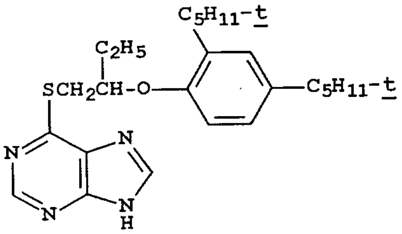


AF:

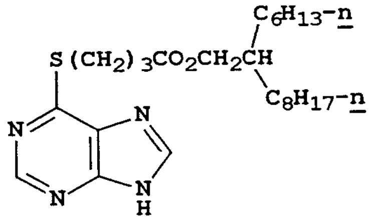
(9.36)



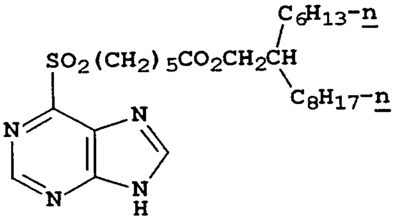
AG:
(7.45)



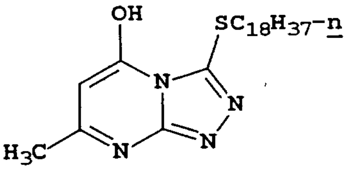
AH:
(8.17)



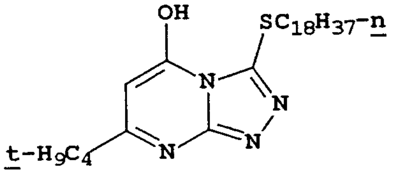
AI:
(6.66)



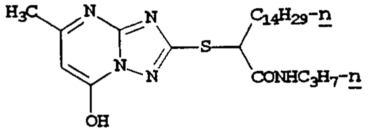
AJ:
(9.35)



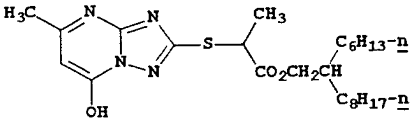
AK:
(10.68)



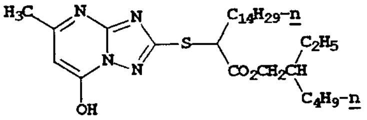
AL:
(7.41)



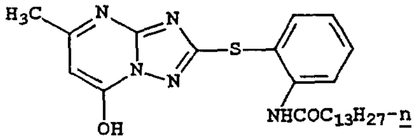
AM:
(8.11)



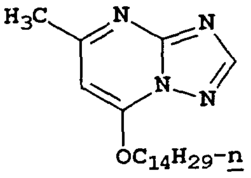
AN:
(10.49)



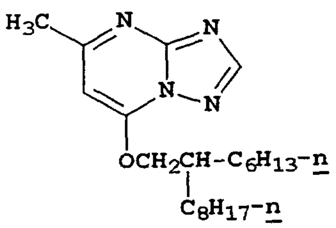
AO:
(7.75)



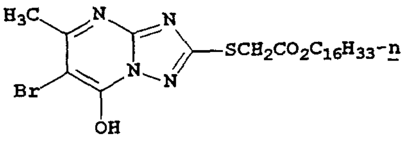
AP:
(6.59)



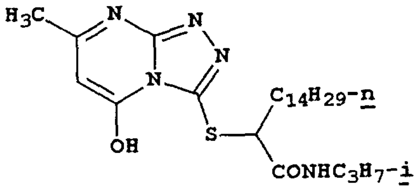
AQ:
(7.52)



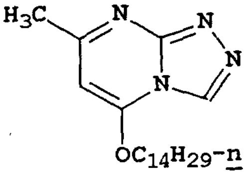
AR:
(8.57)



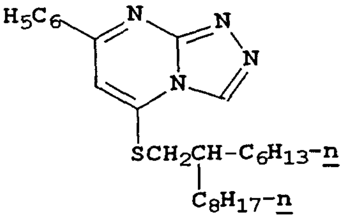
AS:
(6.94)



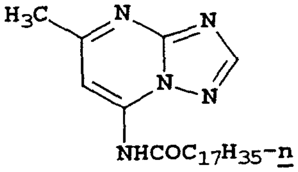
AT:
(6.70)



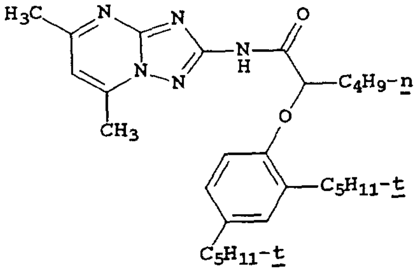
AU:
(9.68)



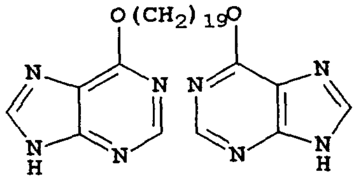
AV:
(7.90)



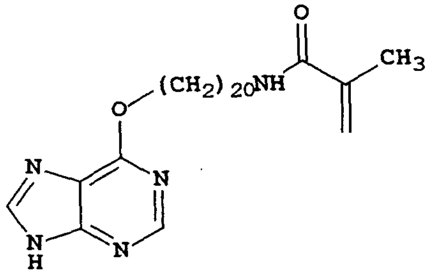
AW:
(8.11)



AX:
(8.37)

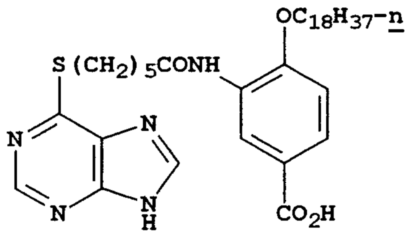


AY:
(8.53)

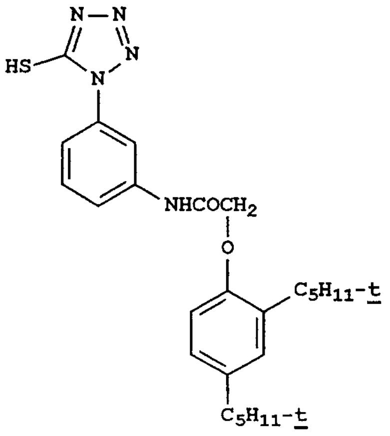


(2:1:1 by weight copolymer with styrene and n-butyl acrylate)

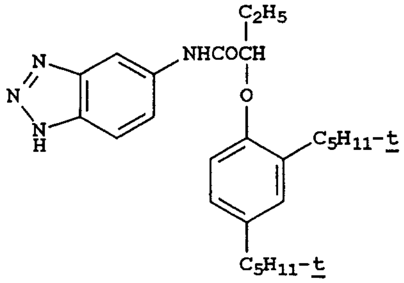
AZ:
(11.08)



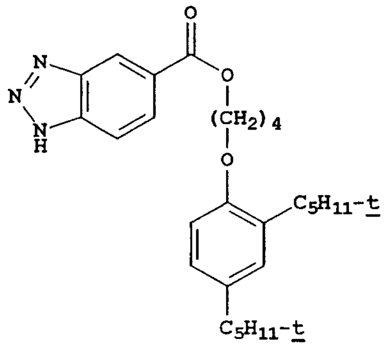
BA:
(7.82)



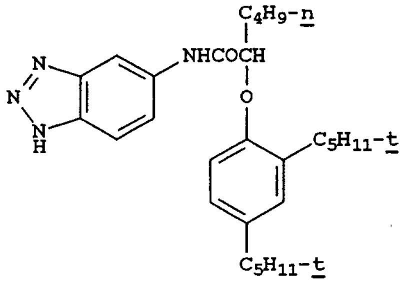
BB:
(7.99)



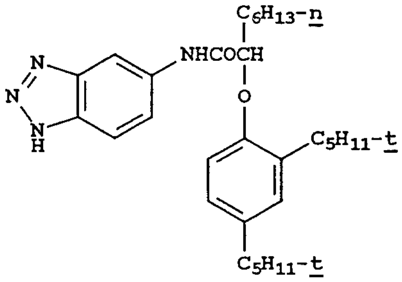
BC:
(8.94)



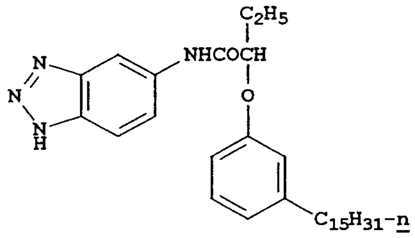
BD:
(9.04)



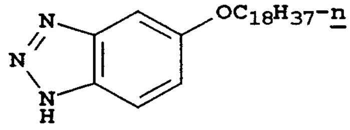
BE:
(10.10)



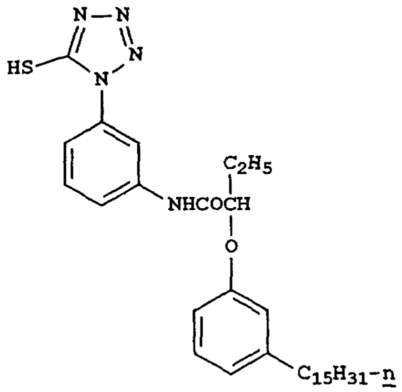
BF:
(11.18)



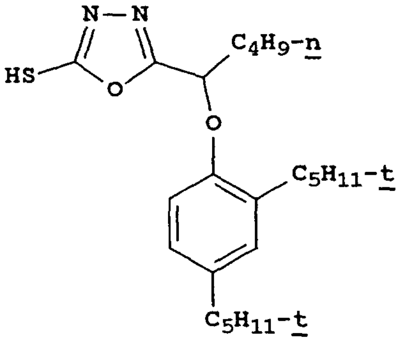
BG:
(10.66)



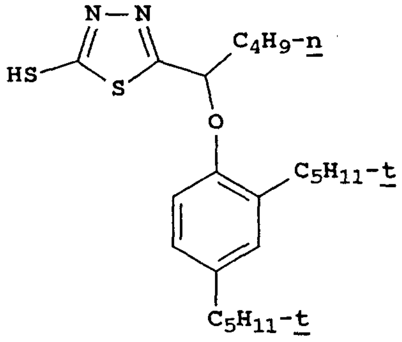
BH:
(11.85)



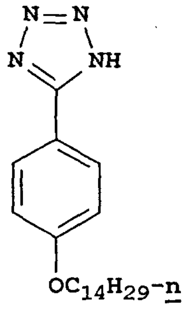
BI:
(7.91)



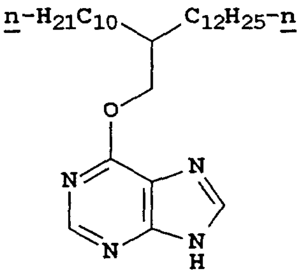
BJ:
(8.23)



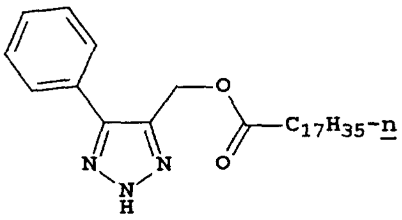
BK:
(8.44)



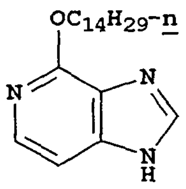
BL:
(12.07)



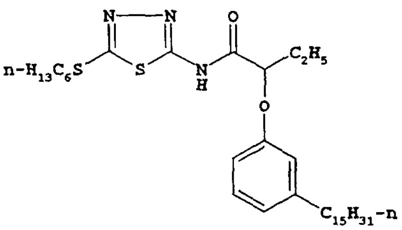
BM:
(10.23)



BN:
(7.76)

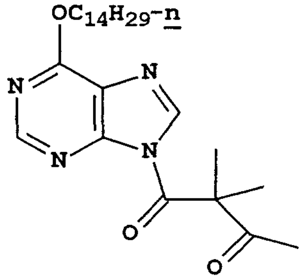


BO:
(13.11)



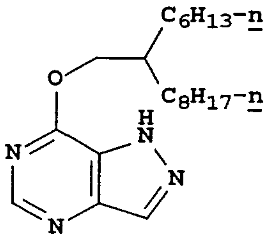
BP

(6.7)



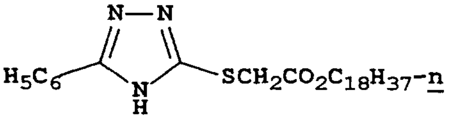
BQ;

(7.84)



BR:

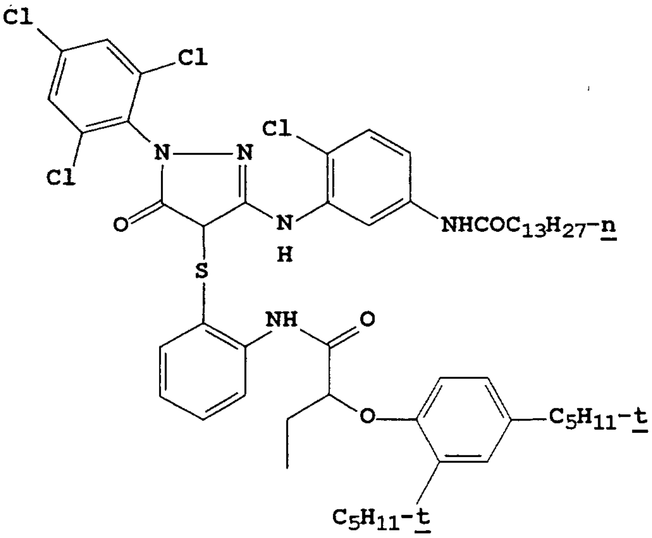
(10.23)



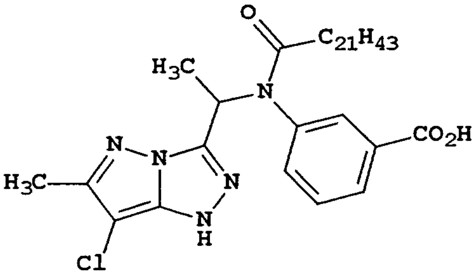
[0038] The materials useful in the invention are not water-soluble in the general sense and cannot be added directly to the silver halide emulsion but are added as a solution in a water miscible organic solvent such as methanol or acetone, or most preferably as a dispersion in order to reduce volatile organic emissions and to avoid uncontrolled precipitate formation. A dispersion incorporates the material in a stable, finely divided state in a hydrophobic organic solvent (often referred to as a coupler solvent or permanent solvent) that is stabilized by suitable surfactants and surface active agents usually in combination with a binder or matrix such as gelatin. The dispersion may contain one or more permanent solvents that dissolve the material and maintain it in a liquid state. Some examples of suitable permanent solvents are tricresylphosphate, N,N-diethyllauramide, N,N-dibutyllauramide, p-dodecylphenol, dibutylphthalate, di-n-butyl sebacate, N-n-butylacetanilide, 9-octadecen-1-ol, *ortho*-methylphenyl benzoate, trioctylamine and 2-ethylhexylphosphate. Permanent solvents can also be described in terms of physical constants such as *alpha*, *beta* and *pi** as defined by M.J. Kamlet, J-L.M. Abboud, M.H. Abraham and R.W. Taft, J. Org Chem, 48, 2877(1983). The preferred permanent solvents used with the materials useful in the invention are those with ClogP of 5.0 or greater and *beta* values of 0.4 or greater or more preferably, *beta* values of 0.5 or greater. Preferred classes of solvents are carbonamides, phosphates, alcohols and esters. When a solvent is present, it is preferred that the weight ratio of compound to solvent be at least 1 to 0.5, or most preferably, at least 1 to 1. The dispersion may require an auxiliary coupler solvent initially to dissolve the component but this is removed afterwards, usually either by evaporation or by washing with additional water. Some examples of suitable auxiliary coupler solvents are ethyl acetate, cyclohexanone and 2-(2-butoxyethoxy)ethyl acetate. The dispersion may also be stabilized by addition of polymeric materials to form stable latexes. Examples of suitable polymers for this use generally contain water-solubilizing groups or have regions of high hydrophilicity. Some examples of suitable dispersing agents or surfactants are Alkanol XC or saponin. The materials useful in the invention may also be dispersed as an admixture with another component of the system such as a coupler or an oxidized developer scavenger so that both are present in the same oil droplet. It is also possible to incorporate the materials useful in the invention as a solid particle dispersion; that is, a slurry or suspension of finely ground (through mechanical means) compound. These solid particle dispersions may be additionally stabilized with surfactants and/or polymeric materials as known in the art. Also, additional permanent solvent may be added to the solid particle dispersion to help increase activity.

[0039] The sensitivity of the human eye is greatest to green light and so, the compounds useful in the invention are most useful with a green sensitive emulsion located in the green record (the layer whose maximum spectral sensitivity to light falls between 500 and 600 nm). The following magenta couplers are particularly beneficial when used in conjunction with the nitrogen heterocycles useful in the invention:

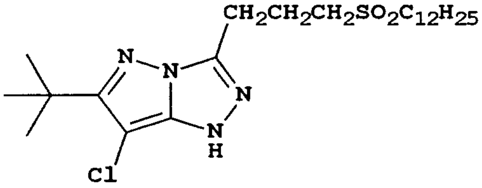
M-1


Cl
Cl
Cl
Cl
N
N
O
N
H
S
NHCOC13H27-n
NH
O
O
C5H11-t
C5H11-t

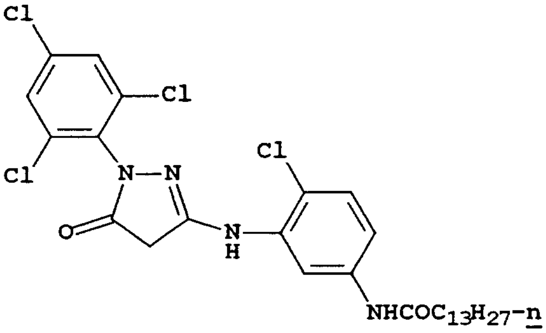
M-2:


O
C21H43
H3C
N
CO2H
N
N
N
H3C
N
H
Cl

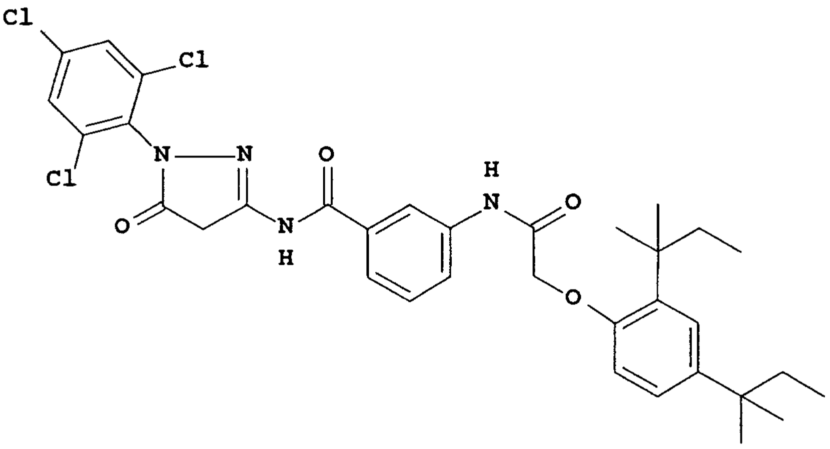
M-3:


CH2CH2CH2SO2C12H25
N
N
N
N
H
Cl

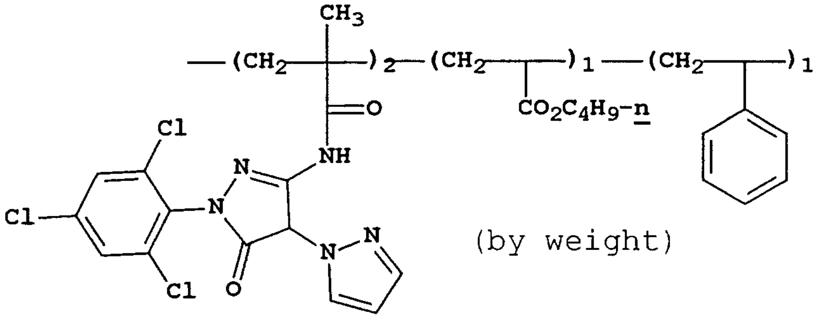
M-4:


Cl
Cl
Cl
Cl
N
N
O
N
H
NHCOC13H27-n

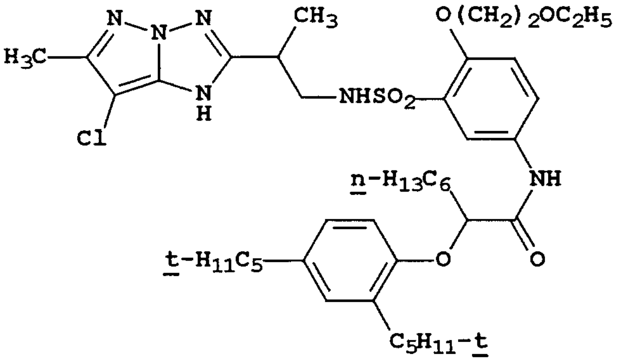
M-5:



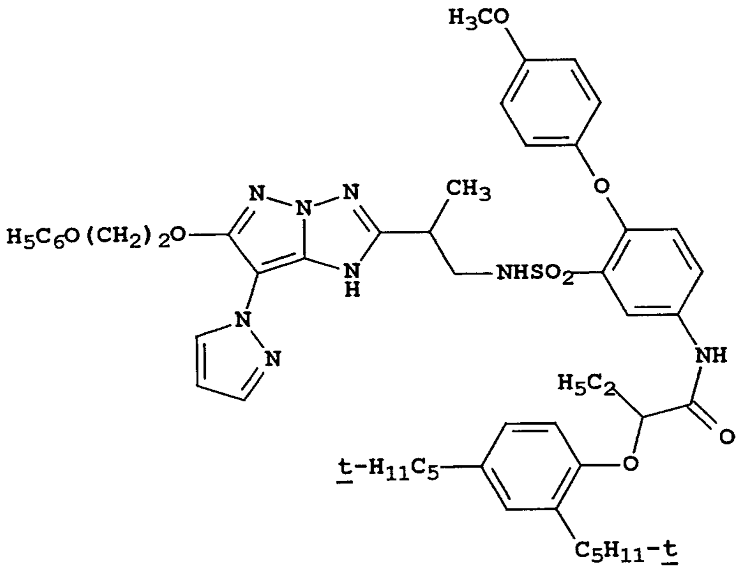
M-6:



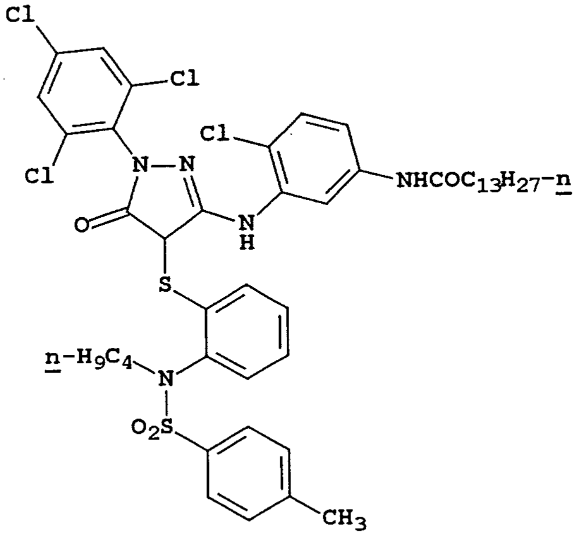
M-7:



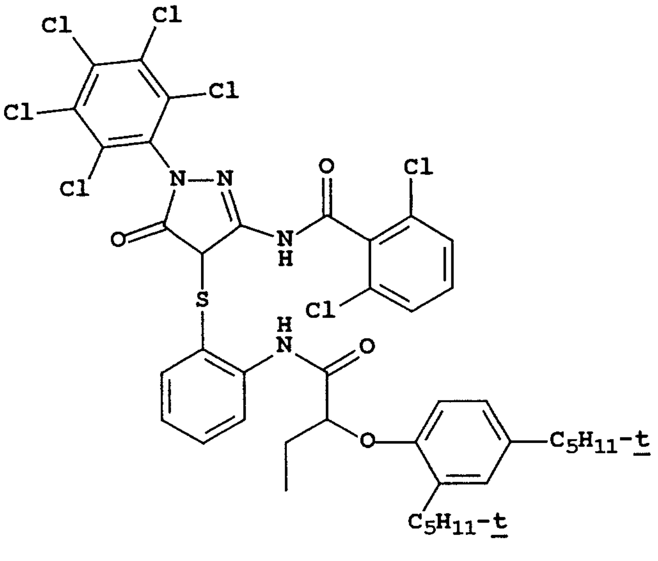
M-8:


H3CO
O
CH3
N
N
N
H5C6O(CH2)2O
N
H
NHSO2
N
N
NH
H5C2
O
O
t-H11C5
C5H11-t

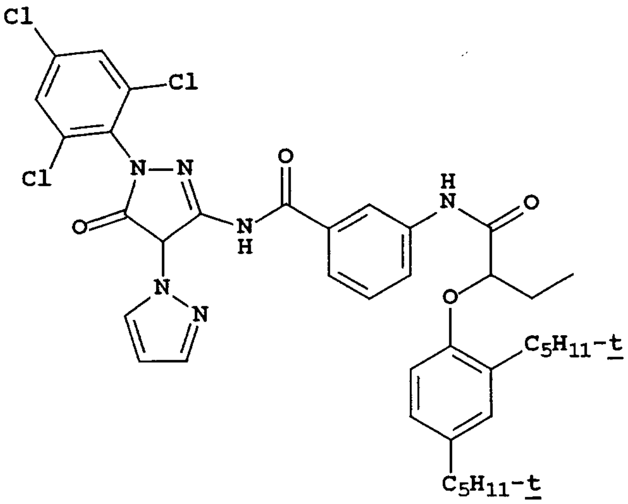
M-9:


Cl
Cl
Cl
Cl
N
N
NHCOC13H27-n
O
N
H
S
n-H9C4
N
O2S
CH3

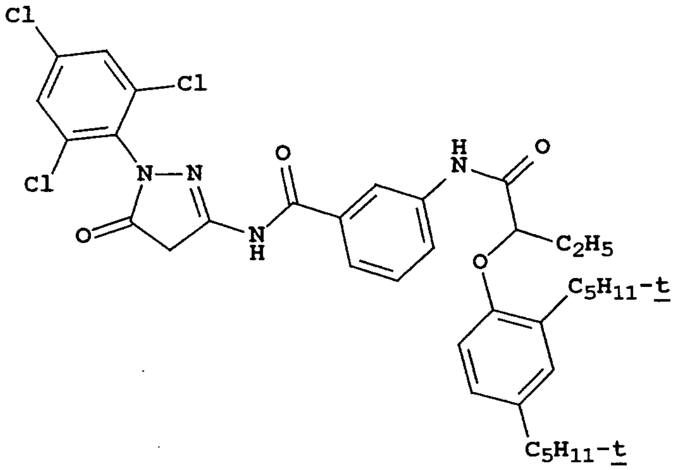
M-10:



M-11:

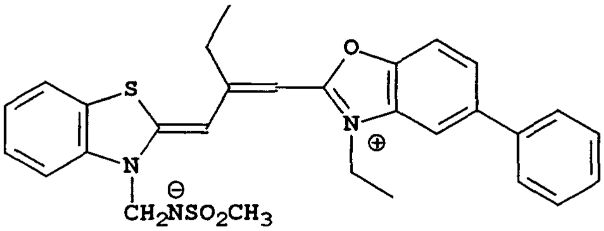


M-12:

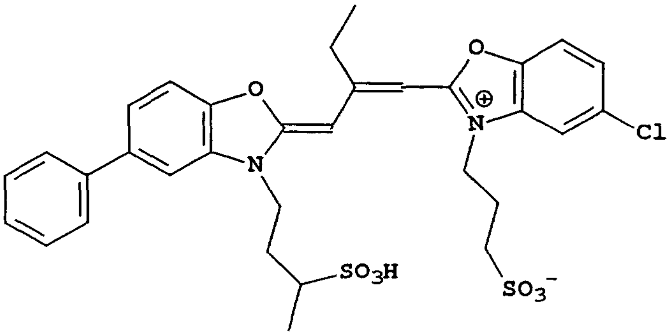


[0040] The following green sensitizing dyes are also particularly beneficial when used in combination with the nitrogen heterocycles useful in the invention:

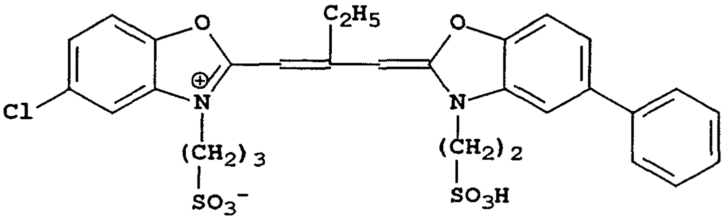
GSD-1



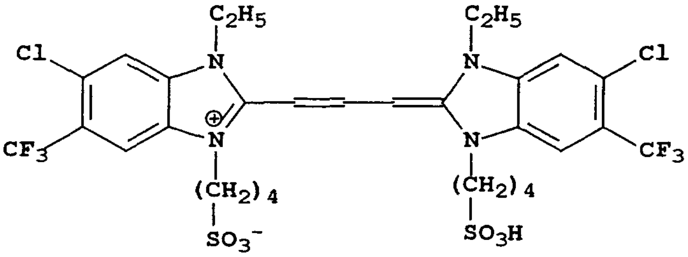
GSD-2



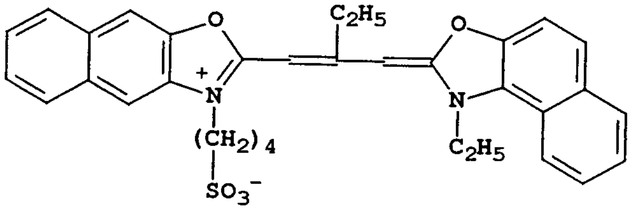
GSD-3:



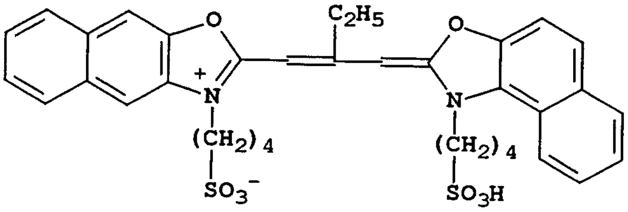
GSD-4:



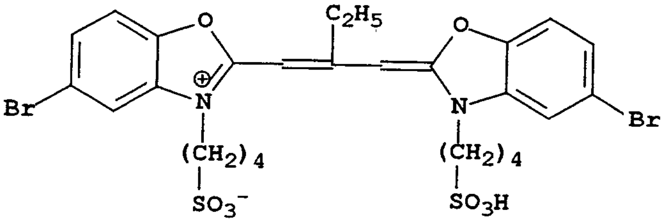
GSD-5:



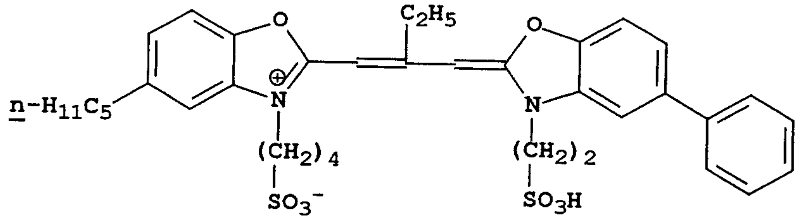
GSD-6:



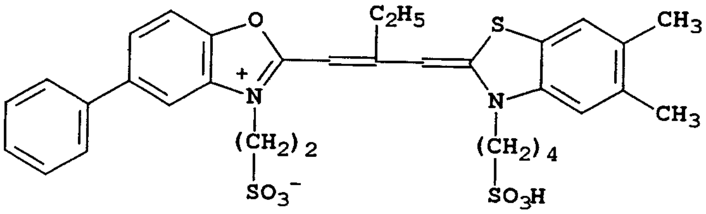
GSD-7:



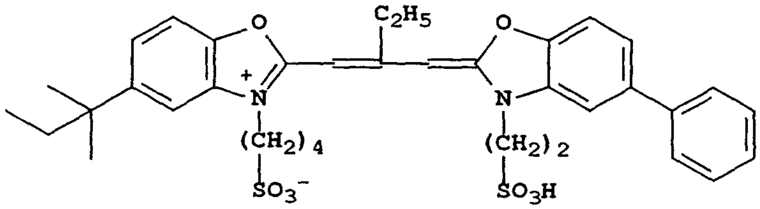
GSD-8:



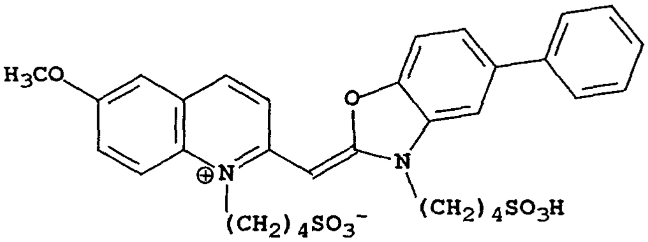
GSD-9:



GSD-10



GSD-11



[0041] The type of light sensitive silver halide emulsion used with the compound useful in the invention may be important to obtain the desired decrease in fog. The silver halide emulsion is suitably a silver iodobromide emulsion, meaning an emulsion that is low in chloride. By low in chloride, it is meant that there should be no more than 20 mol %. More suitably, there is present in the layer no more than 10 mol % chloride, and typically no more than 1 mol % chloride. The emulsion suitably contains at least 0.01 mol % iodide, or more preferably, at least 0.5 mol % iodide or most preferably, at least 1 mol % iodide. The benefit of the fog decrease is most apparent in combination with larger sized emulsions that are associated with increased fog. Thus, it is preferred that the compounds useful in the invention are used with emulsions that have an equivalent circular diameter of at least 0.6 micrometer, or more preferably, at least 0.8 micrometer, or most preferably, at least 1.0 micrometer.

[0042] The compounds useful in the invention are also particularly useful when used in film elements that contain low overall silver levels. Thus, films containing 9 g/m^2 of total silver or less, or more preferably 5.4 g/m^2 or less or even 4.3 g/m^2 or less benefit from the use of the compounds useful in the invention.

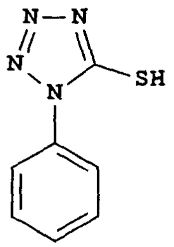
[0043] In order to control and maintain granularity over a wide exposure range, it is a common practice to divide an individual color record into separate layers, each containing silver halide emulsions of different degree of sensitivity to the same color of light and so, each can have a different propensity to fog. While the compound useful in the invention is most useful in the most light sensitive layer (which generally has the highest fog level), it can be used in more than one record that is sensitive to the same color of light. For example, in a color record that is split into three layers of different relative sensitivity; fast (F), mid (M) or slow (S), the compound can be used in each layer only or in any combination ; i.e. F+M, F+M+S, F+S, etc. It is not necessary that these layers be adjacent; that is, they may have interlayers or even imaging layers that are sensitive to other colors located between them. In addition, although the most light sensitive layer is typically located in the film structure closest to the exposure source and farthest from the support, the compounds useful in the invention allow for alternative locations of the layers; for example, a more light sensitive layer containing the compound useful in the invention may be located below (farther from the exposing source) than a less sensitive layer. It is also possible to use the compounds useful in the invention in more than one color record at a time.

[0044] Moreover, when a number of layers of the same spectral sensitivity but of differing degrees of sensitivity to light are used, it is known that overall granularity can be minimized by using a smaller molar amount of dye-forming coupler than silver in the layers of higher sensitivity. Thus, it is preferred that the layers containing the compound useful in the invention additionally contain less than a stoichiometric amount of total dye forming coupler(s) relative to the amount of silver contained in the same layer. A suitable molar ratio of dye-forming coupler(s) to silver in the layer containing the compound useful in the invention would be less than 0.5. Most preferred would be a ratio of 0.2 or even 0.1 or less.

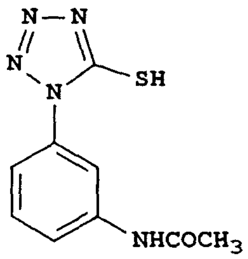
[0045] It is known that film elements can contain silver halide emulsions in one layer that have maximum sensitivities that are separated or shifted from emulsions in other layers that are sensitive to the same color of light (for example, a layer containing an emulsion with maximum sensitivity at ~ 530 nm whereas another layer contains a different green light sensitive emulsion which is most sensitive at ~ 550 nm) are useful for increasing the amount of interimage and improving color reproduction. The layer containing the emulsions with shifted sensitivities may not contain any image couplers at all, but rather only inhibitor releasing couplers (DIRs or DIARs (Development Inhibitor Anchimeric Releasing couplers)) or colored masking couplers. The compounds useful in the invention are particularly useful in this type of application since they allow for the improved color reproduction and Dmin while maintaining the speed of the element.

[0046] The compounds useful in the invention can be used in combination with any of the other antifoggants or scavengers known in the art to be useful in controlling Dmin or fog. Specific examples of scavengers for oxidized developers would be 2,5-di-t-octylhydroquinone, 2-(3,5-bis-(2-hexyldodecylamido)benzamido)-1,4-hydroquinone, 2,4-(4-dodecyloxybenzenesulfonamido)phenol, 2,5-dihydroxy-4-(1-methylheptadecyl)benzenesulfonic acid or 2,5-di-s-dodecylhydroquinone. Specific examples of useful antifoggants are compounds AF-1 to AF-8 whose structures are shown below as well as 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene:

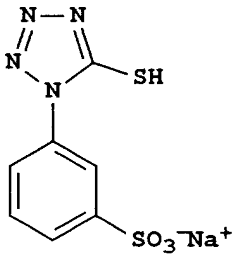
AF-1



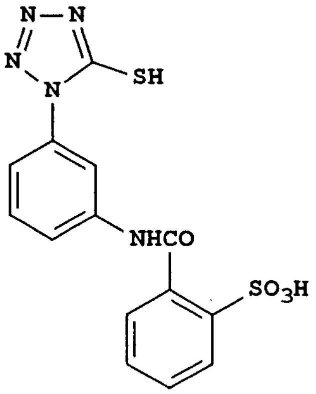
AF-2:



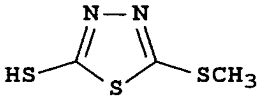
AF-3:



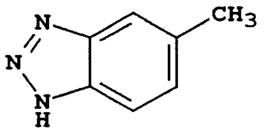
AF-4:



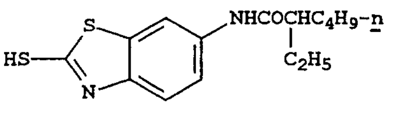
AF-5:



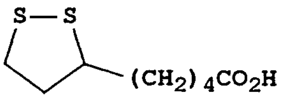
AF-6:



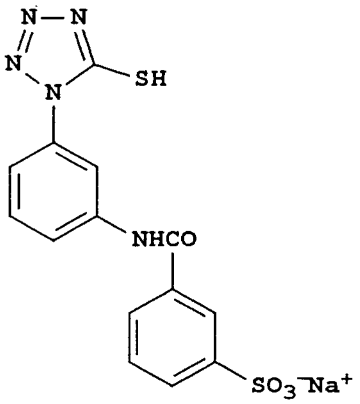
AF-7:



AF-8:



AF-9



[0047] Unless otherwise specifically stated or when the term "group" is used, it is intended throughout this specification, when a substituent group contains a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned, so long as the group does not destroy properties necessary for photographic utility. Suitably, a substituent group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine, iodine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain or cyclic alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-t-pentylphenoxy)propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, sec-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentylphenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)tetradecanamido, 2-oxopyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-tolylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-tolylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-tolylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-t-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-t-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-tolylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfmyl, and *p*-tolylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1-(N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

[0048] If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups, etc. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

[0049] To control the migration of various components, it may be desirable to include a high molecular weight or polymeric backbone containing hydrophobic or "ballast" group in molecules. Representative ballast groups include substituted or unsubstituted alkyl or aryl groups containing 8 to 48 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxcarbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

[0050] Photographic elements herein may be black and white or color elements. As used herein, the term "color photographic element" means any element containing a light-sensitive silver halide emulsion layer containing an image dye-forming coupler. They can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer. A single color element may comprise a combination of couplers in one or more common layers which upon processing together form a monocolor, including black or gray, (so-called chromogenic black and white) dye image.

[0051] A typical color photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, or subbing layers.

[0052] If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in *Research Disclosure,* November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, and as described in Hatsumi Kyoukai Koukai Gihou No. 94-6023, published March 15, 1994, available from the Japanese Patent Office. When it is desired to employ the inventive materials in a small format film, Research Disclosure, June 1994, Item 36230, provides suitable embodiments.

[0053] In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, September 1996, Item 38957, available as described above, which is referred to herein by the term "Research Disclosure". The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

[0054] Except as provided, the silver halide emulsion containing elements employed in this invention can be either negative-working or positive-working as indicated by the type of processing instructions (i.e. color negative, reversal, or direct positive processing) provided with the element. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through V. Various additives such as UV dyes, brighteners, antifoggants, stabilizers, light absorbing and scattering materials, and physical property modifying addenda such as hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections II and VI through VIII. Color materials are described in Sections X through XIII. Suitable methods for incorporating couplers and dyes, including dispersions in organic solvents, are described in Section X(E). Scan facilitating is described in Section XIV. Supports, exposure, development systems, and processing methods and agents are described in Sections XV to XX. The information contained in the September 1994 Research Disclosure, Item No. 36544 referenced above, is updated in the September 1996 Research Disclosure, Item No. 38957. Certain desirable photographic elements and processing steps, including those useful in conjunction with color reflective prints, are described in Research Disclosure, Item 37038, February 1995.

[0055] Coupling-off groups are well known in the art. Such groups can determine the chemical equivalency of a coupler, i.e., whether it is a 2-equivalent or a 4-equivalent coupler, or modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, or color correction.

[0056] The presence of hydrogen at the coupling site provides a 4-equivalent coupler, and the presence of another coupling-off group usually provides a 2-equivalent coupler. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, hetero-oxy, sulfonyloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercaptotetrazole, benzothiazole, mercaptopropionic acid, phosphonyloxy, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Pat. Nos. 2,455,169, 3,227,551, 3,432,521, 3,476,563, 3,617,291, 3,880,661, 4,052,212 and 4,134,766; and in UK. Patents and published application Nos. 1,466,728, 1,531,927, 1,533,039, 2,006,755A and 2,017,704A

[0057] Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as:

> "Farbkuppler-eine Literature Ubersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961) as well as in U.S. Patent Nos. 2,367,531; 2,423,730; 2,474,293; 2,772,162; 2,895,826; 3,002,836; 3,034,892; 3,041,236; 4,333,999; 4,746,602; 4,753,871; 4,770,988; 4,775,616; 4,818,667; 4,818,672; 4,822,729; 4,839,267; 4,840,883; 4,849,328; 4,865,961; 4,873,183; 4,883,746; 4,900,656; 4,904,575; 4,916,051; 4,921,783; 4,923,791; 4,950,585; 4,971,898; 4,990,436; 4,996,139; 5,008,180; 5,015,565; 5,011,765; 5,011,766; 5,017,467; 5,045,442; 5,051,347; 5,061,613; 5,071,737; 5,075,207; 5,091,297; 5,094,938; 5,104,783; 5,178,993; 5,813,729; 5,187,057; 5,192,651; 5,200,305 5,202,224; 5,206,130; 5,208,141; 5,210,011; 5,215,871; 5,223,386; 5,227,287; 5,256,526; 5,258,270; 5,272,051; 5,306,610; 5,326,682; 5,366,856; 5,378,596; 5,380,638; 5,382,502; 5,384,236; 5,397,691; 5,415,990; 5,434,034; 5,441,863; EPO 0 246 616;
> EPO 0 250 201; EPO 0 271 323; EPO 0 295 632; EPO 0 307 927;
> EPO 0 333 185; EPO 0 378 898; EPO 0 389 817; EPO 0 487 111;
> EPO 0 488 248; EPO 0 539 034; EPO 0 545 300; EPO 0 556 700;
> EPO 0 556 777; EPO 0 556 858; EPO 0 569 979; EPO 0 608 133;
> EPO 0 636 936; EPO 0 651 286; EPO 0 690 344; German OLS 4,026,903; German OLS 3,624,777. and German OLS 3,823,049. Typically such couplers are phenols, naphthols, or pyrazoloazoles.

[0058] Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as:

> "Farbkuppler-eine Literature Ubersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961) as well as U.S. Patents 2,311,082 and 2,369,489; 2,343,701; 2,600,788; 2,908,573; 3,062,653; 3,152,896; 3,519,429; 3,758,309; 3,935,015; 4,540,654; 4,745,052; 4,762,775; 4,791,052; 4,812,576; 4,835,094; 4,840,877; 4,845,022; 4,853,319; 4,868,099; 4,865,960; 4,871,652; 4,876,182; 4,892,805; 4,900,657; 4,910,124; 4,914,013; 4,921,968; 4,929,540; 4,933,465; 4,942,116; 4,942,117; 4,942,118; U.S. Patent 4,959,480; 4,968,594; 4,988,614; 4,992,361; 5,002,864; 5,021,325; 5,066,575; 5,068,171; 5,071,739; 5,100,772; 5,110,942; 5,116,990; 5,118,812; 5,134,059; 5,155,016; 5,183,728; 5,234,805; 5,235,058; 5,250,400; 5,254,446; 5,262,292; 5,300,407; 5,302,496; 5,336,593; 5,350,667; 5,395,968; 5,354,826; 5,358,829; 5,368,998; 5,378,587; 5,409,808; 5,411,841; 5,418,123; 5,424,179; EPO 0 257 854; EPO 0 284 240; EPO 0 341 204; EPO 347,235; EPO 365,252; EPO 0 422 595; EPO 0 428 899; EPO 0 428 902; EPO 0 459 331; EPO 0 467 327; EPO 0 476 949; EPO 0 487 081; EPO 0 489 333; EPO 0 512 304; EPO 0 515 128; EPO 0 534 703;
> EPO 0 554 778; EPO 0 558 145; EPO 0 571 959; EPO 0 583 832;
> EPO 0 583 834; EPO 0 584 793; EPO 0 602 748; EPO 0 602 749;
> EPO 0 605 918; EPO 0 622 672; EPO 0 622 673; EPO 0 629 912;
> EPO 0 646 841, EPO 0 656 561; EPO 0 660 177; EPO 0 686 872; WO 90/10253;
> WO 92/09010; WO 92/10788; WO 92/12464; WO 93/01523; WO 93/02392;
> WO 93/02393; WO 93/07534; UK Application 2,244,053; Japanese Application 03192-350; German OLS 3,624,103; German OLS 3,912,265; and German OLS 40 08 067. Typically such couplers are pyrazolones, pyrazoloazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents.

[0059] Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as:

> "Farbkuppler-eine Literature Ubersicht," published in Agfa Mitteilungen; Band III; pp. 112-126 (1961); as well as U.S. Patent 2,298,443; 2,407,210; 2,875,057; 3,048,194; 3,265,506; 3,447,928; 4,022,620; 4,443,536; 4,758,501; 4,791,050; 4,824,771; 4,824,773; 4,855,222; 4,978,605; 4,992,360; 4,994,361; 5,021,333; 5,053,325; 5,066,574; 5,066,576; 5,100,773; 5,118,599; 5,143,823; 5,187,055; 5,190,848; 5,213,958; 5,215,877; 5,215,878; 5,217,857; 5,219,716; 5,238,803; 5,283,166; 5,294,531; 5,306,609; 5,328,818; 5,336,591; 5,338,654; 5,358,835; 5,358,838; 5,360,713; 5,362,617; 5,382,506; 5,389,504; 5,399,474;. 5,405,737; 5,411,848; 5,427,898; EPO 0 327 976; EPO 0 296 793; EPO 0 365 282;

EPO 0 379 309; EPO 0 415 375; EPO 0 437 818; EPO 0 447 969;
EPO 0 542 463; EPO 0 568 037; EPO 0 568 196; EPO 0 568 777;
EPO 0 570 006; EPO 0 573 761; EPO 0 608 956; EPO 0 608 957; and
EPO 0 628 865. Such couplers are typically open chain ketomethylene compounds.

[0060] Couplers that form colorless products upon reaction with oxidized color developing agent are described in such representative patents as:
UK. 861,138; U.S. Pat. Nos. 3,632,345; 3,928,041; 3,958,993 and 3,961,959. Typically such couplers are cyclic carbonyl containing compounds that form colorless products on reaction with an oxidized color developing agent.

[0061] Couplers that form black dyes upon reaction with oxidized color developing agent are described in such representative patents as U.S. Patent Nos. 1,939,231; 2,181,944; 2,333,106; and 4,126,461; German OLS No. 2,644,194 and German OLS No. 2,650,764. Typically, such couplers are resorcinols or m-aminophenols that form black or neutral products on reaction with oxidized color developing agent.

[0062] In addition to the foregoing, so-called "universal" or "washout" couplers may be employed. These couplers do not contribute to image dye-formation. Thus, for example, a naphthol having an unsubstituted carbamoyl or one substituted with a low molecular weight substituent at the 2- or 3- position may be employed. Couplers of this type are described, for example, in U.S. Patent Nos. 5,026,628, 5,151,343, and 5,234,800.

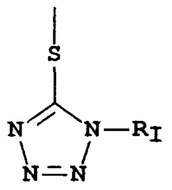
[0063] It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may contain solubilizing groups such as described in U.S. Patent 4,482,629. The coupler may also be used in association with "wrong" colored couplers (e.g. to adjust levels of interlayer correction) and, in color negative applications, with masking couplers such as those described in EP 213.490; Japanese Published Application 58-172,647; U.S. Patent Nos. 2,983,608; 4,070,191; and 4,273,861; German Applications DE 2,706,117 and DE 2,643,965; UK. Patent 1,530,272; and Japanese Application 58-113935. The masking couplers may be shifted or blocked, if desired.

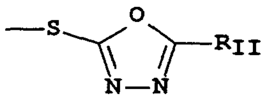
[0064] The invention materials may be used in association with materials that release Photographically Useful Groups (PUGS) that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; UK. Patent 2,131,188); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

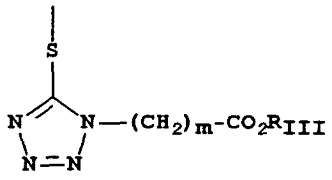
[0065] The invention materials may also be used in combination with filter dye layers comprising yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions or Carey-Lea (yellow colored) silver. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

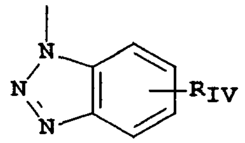
[0066] The invention materials may further be used in combination with image-modifying compounds that release PUGS such as "Developer Inhibitor-Releasing" compounds (DIRs). DIRs useful in conjunction with the compositions useful in the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

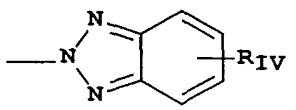
[0067] Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography, " C.R. Barr, J.R. Thirtle and P.W. Vittum in *Photographic Science and Engineering,* Vol. 13, p. 174 (1969). Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) that also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isoindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzodiazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptothiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles, mercaptooxathiazoles, telleurotetrazoles or benzisodiazoles. In a preferred embodiment, the inhibitor moiety or group is selected from the following formulas:







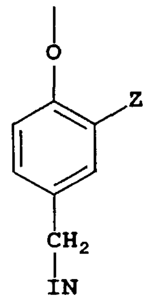


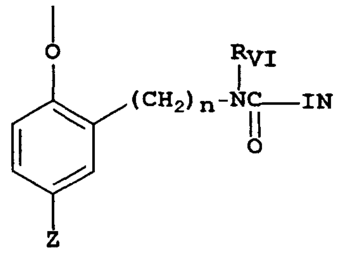


wherein R_I is selected from the group consisting of straight and branched alkyls of from 1 to 8 carbon atoms, benzyl, phenyl, and alkoxy groups and such groups containing none, one or more than one such substituent; R_{II} is selected from R_I and $-SR_I$; R_{III} is a straight or branched alkyl group of from 1 to 5 carbon atoms and m is from 1 to 3; and R_{IV} is selected from the group consisting of hydrogen, halogens and alkoxy, phenyl and carbonamido groups, $-COOR_V$ and-$NHCOOR_V$ wherein R_V is selected from substituted and unsubstituted alkyl and aryl groups.

[0068] Although it is typical that the coupler moiety included in the developer inhibitor-releasing coupler forms an image dye corresponding to the layer in which it is located, it may also form a different color as one associated with a different film layer. It may also be useful that the coupler moiety included in the developer inhibitor-releasing coupler forms colorless products and/or products that wash out of the photographic material during processing (so-called "universal" couplers).

[0069] A compound such as a coupler may release a PUG directly upon reaction of the compound during processing, or indirectly through a timing or linking group. A timing group produces the time-delayed release of the PUG such groups using an intramolecular nucleophilic substitution reaction (U.S. 4,248,962); groups utilizing an electron transfer reaction along a conjugated system (U.S. 4,409,323; 4,421,845; 4,861,701, Japanese Applications 57-188035; 58-98728; 58-209736; 58-209738); groups that function as a coupler or reducing agent after the coupler reaction (U. S. 4,438,193; U.S. 4,618,571) and groups that combine the features described above. It is typical that the timing group is of one of the formulas:



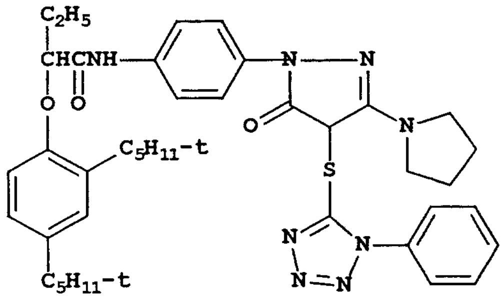


wherein IN is the inhibitor moiety, Z is selected from the group consisting of nitro, cyano, alkylsulfonyl; sulfamoyl ($-SO_2NR_2$); and sulfonamido ($-NRSO_2R$) groups; n is 0 or 1; and R_{VI} is selected from the group consisting of substituted and unsubstituted alkyl and phenyl groups. The oxygen atom of each timing group is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

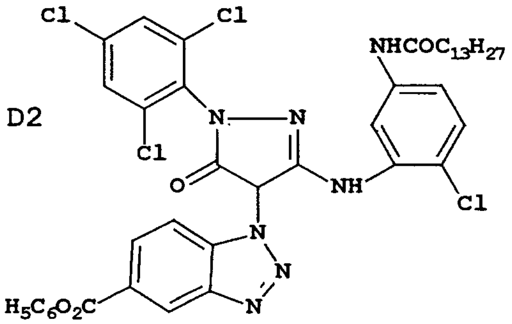
[0070] The timing or linking groups may also function by electron transfer down an unconjugated chain. Linking groups are known in the art under various names. Often they have been referred to as groups capable of utilizing a hemiacetal or iminoketal cleavage reaction or as groups capable of utilizing a cleavage reaction due to ester hydrolysis such as U.S. 4,546,073. This electron transfer down an unconjugated chain typically results in a relatively fast decomposition and the production of carbon dioxide, formaldehyde, or other low molecular weight by-products. The groups are exemplified in EP 464,612, EP 523,451, U.S. 4,146,396, Japanese Kokai 60-249148 and 60-249149.

[0071] Suitable developer inhibitor-releasing couplers that may be included in photographic light sensitive emulsion layer include, but are not limited to, the following:

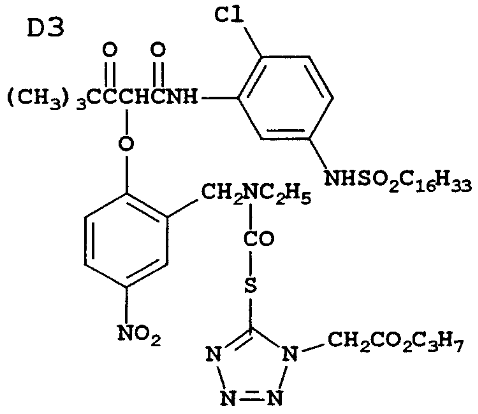
D1



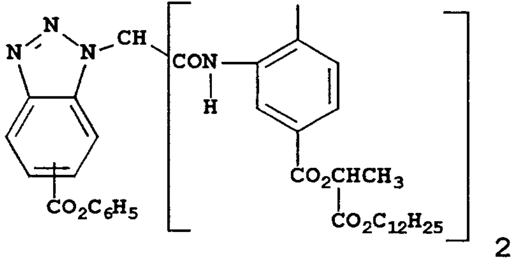
D2



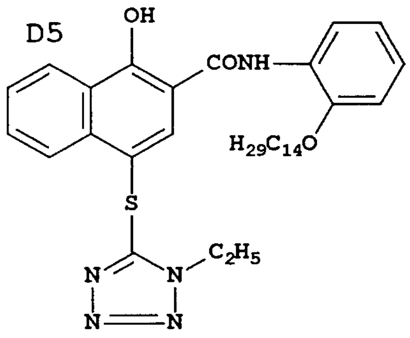
D3



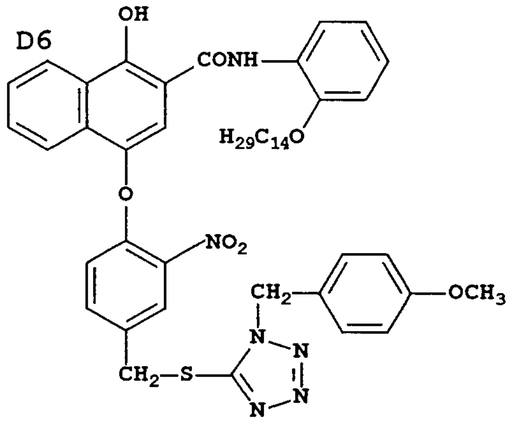
D4



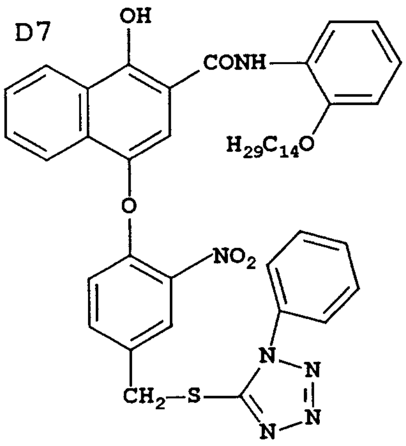
D5



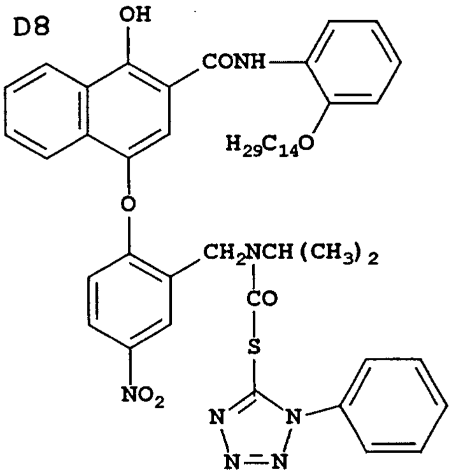
D6



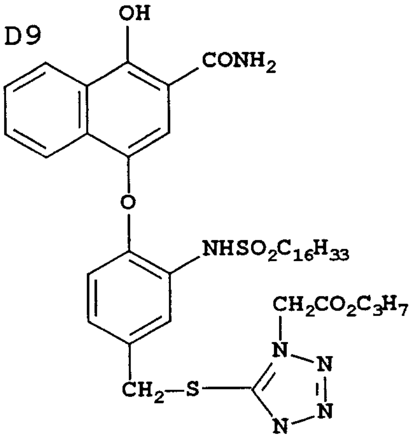
D7



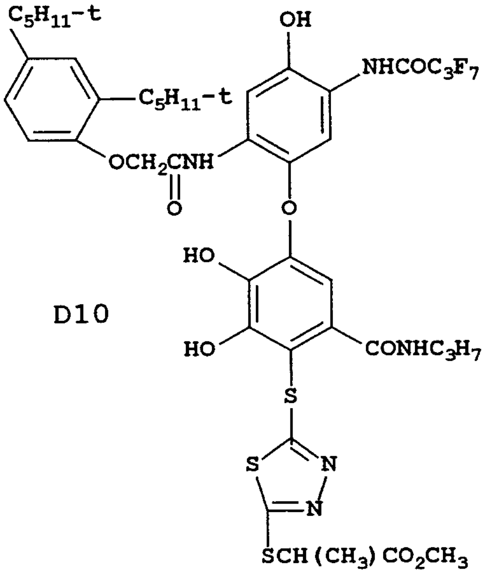
D8



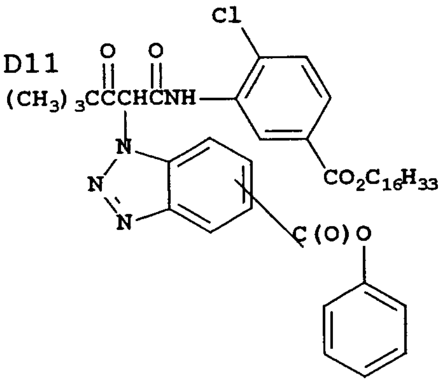
D9



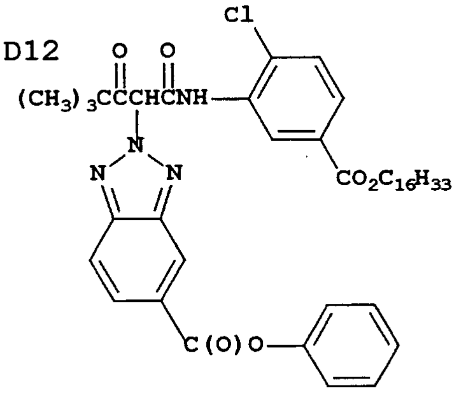
D10



D11



D12



[0072] Especially useful in this invention are tabular grain silver halide emulsions. Tabular grains are those having two parallel major crystal faces and having an aspect ratio of at least 2. The term "aspect ratio" is the ratio of the equivalent circular diameter (ECD) of a grain major face divided by its thickness (t). The major faces of the tabular grains can lie in either {111} or {100} crystal planes. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micrometer (0.5 micrometer for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

$$T = ECD/t^2$$

where

ECD is the average equivalent circular diameter of the tabular grains in micrometers and
t is the average thickness in micrometers of the tabular grains.

[0073] The average useful ECD of photographic emulsions can range up to 10 micrometers, although in practice emulsion ECDs seldom exceed 4 micrometers. Since both photographic speed and granularity increase with increasing ECDs, it is generally preferred to employ the smallest tabular grain ECDs compatible with achieving aim speed requirements.

[0074] Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin (t < 0.2 micrometer) tabular grains. To achieve the lowest levels of granularity it is preferred that aim tabular grain projected areas be satisfied with ultrathin (t < 0.07 micrometer) tabular grains. Tabular grain thicknesses typically range down to 0.02 micrometer. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek *et al.* U.S. Patent 4,672,027 reports a 3 mol percent iodide tabular grain silver bromoiodide emulsion having a grain thickness of 0.017 micrometer. Ultrathin tabular grain high chloride emulsions are disclosed by Maskasky U.S. 5,217,858.

[0075] As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions, tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions, tabular grains satisfying the thickness criteria above account for at least 90 percent of total grain projected area.

[0076] Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following Research Disclosure, Item 22534, January 1983, published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire P010 7DD, England; U.S. Patent Nos. 4,439,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616. Tabular grain emulsions consisting predominantly of silver chloride are useful and are described, for example, in U.S. 5,310,635; 5,320,938; and 5,356,764.

[0077] In their most widely used form tabular grain emulsions are high bromide {111} tabular grain emulsions. Such emulsions are illustrated by Kofron et al U.S. Patent 4,439,520, Wilgus et al U.S. Patent 4,434,226, Solberg et al U.S. Patent 4,433,048, Maskasky U.S. Patents 4,435,501, 4,463,087 and 4,173,320, Daubendiek et al U.S. Patents 4,414,310 and 4,914,014, Sowinski et al U.S. Patent 4,656,122, Piggin et al U.S. Patents 5,061,616 and 5,061,609, Tsaur et al U.S. Patents 5,147,771, 5,147,772, 5,147,773, 5,171,659 and 5,252,453, Black et al 5,219,720 and 5,334,495, Delton U.S. Patents 5,310,644, 5,372,927 and 5,460,934, Wen U.S. Patent 5,470,698, Fenton et al U.S. Patent 5,476,760, Eshelman et al U.S. Patents 5,612,175 and 5,614,359, and Irving et al U.S. Patent 5,667,954.

[0078] Ultrathin high bromide {111} tabular grain emulsions are illustrated by Daubendiek et al U.S. Patents 4,672,027, 4,693,964, 5,494,789, 5,503,971 and 5,576,168, Antoniades et al U.S. Patent 5,250,403, Olm et al U.S. Patent 5,503,970, Deaton et al U.S. Patent 5,582,965, and Maskasky U.S. Patent 5,667,955.

[0079] High bromide {100} tabular grain emulsions are illustrated by Mignot U.S. Patents 4,386,156 and 5,386,156.

[0080] High chloride {111} tabular grain emulsions are illustrated by Wey U.S. Patent 4,399,215, Wey et al U.S. Patent 4,414,306, Maskasky U.S. Patents 4,400,463, 4,713,323, 5,061,617, 5,178,997, 5,183,732, 5,185,239, 5,399,478 and 5,411,852, and Maskasky et al U.S. Patents 5,176,992 and 5,178,998. Ultrathin high chloride {111} tabular grain emulsions are illustrated by Maskasky U.S. Patents 5,271,858 and 5,389,509.

[0081] High chloride {100} tabular grain emulsions are illustrated by Maskasky U.S. Patents 5,264,337, 5,292,632, 5,275,930 and 5,399,477, House et al U.S. Patent 5,320,938, Brust et al U.S. Patent 5,314,798, Szajewski et al U.S.

Patent 5,356,764, Chang et al U.S. Patents 5,413,904 and 5,663,041, Oyamada U.S. Patent 5,593,821, Yamashita et al U.S. Patents 5,641,620 and 5,652,088, Saitou et al U.S. Patent 5,652,089, and Oyamada et al U.S. Patent 5,665,530. Ultrathin high chloride {100} tabular grain emulsions can be prepared by nucleation in the presence of iodide, following the teaching of House et al and Chang et al, cited above.

[0082] Further description of tabular grain emulsions and their preparation and modification used with the compounds useful in the invention can be found in *Research Disclosure,* Vol. 365 (1994) Item 36544, Section I. Emulsion grains and their preparation. Dopants for the tabular grains that may be utilized in the invention include those disclosed in February 1995 *Research Disclosure* Item 37038, Section XV (B).

[0083] Subsequent to their preparation the emulsions can be prepared for photographic use as described by *Research Disclosure,* Item 36544, cited above: I. Emulsion grains and their preparation, E. Blends, layers and performance categories; II. Vehicles, vehicle extenders, vehicle like addenda and vehicle related addenda; III. Emulsion washing. The emulsions or the photographic elements in which they are incorporated can additionally include one or more of the following features illustrated by *Research Disclosure,* Item 36544, cited above: VI. UV dyes, optical brighteners, luminescent dyes; VII. Antifoggants and stabilizers; VIII. Absorbing and scattering materials; IX. Coating physical property modifying addenda; X. Dye image formers and modifiers; XI. Layers and layers arrangement; XII. Features applicable only to color negative; XIII. Features applicable only to color positive; XIV. Scan facilitating features; and XV. Supports.

[0084] The emulsions can be surface-sensitive emulsions, i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent. Tabular grain emulsions of the latter type are illustrated by Evans et al. U.S. 4,504,570.

[0085] Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a color-developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye. The exposure and processing of photographic elements incorporating the emulsion useful in the invention can take any conventional form, illustrated by *Research Disclosure,* Item 36544, cited above. XVI. Exposure; XVIII Chemical development system; XIX. Development; and XX. Desilvering, washing, rinsing and stabilizing.

[0086] With negative-working silver halide, the processing step described above provides a negative image. One type of such element, referred to as a color negative film, is designed for image capture. Speed (the sensitivity of the element to low light conditions) is usually critical to obtaining sufficient image in such elements. Such elements are typically silver bromoiodide emulsions and may be processed, for example, in known color negative processes such as the Kodak C-41™ process as described in The British Journal of Photography Annual of 1988, pages 191-198. If a color negative film element is to be subsequently employed to generate a viewable projection print as for a motion picture, a process such as the Kodak ECN-2™ process described in the H-24 Manual available from Eastman Kodak Co. may be employed to provide the color negative image on a transparent support. Color negative development times are typically 3 minutes 15 seconds. The photographic element useful in the invention can be incorporated into exposure structures intended for repeated use or exposure structures intended for limited use, variously referred to by names such as "single use cameras", "lens with film", or "photosensitive material package units".

[0087] A reversal element is capable of forming a positive image without optical printing. To provide a positive (or reversal) image, the color development step is preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Such reversal emulsions are typically sold with instructions to process using a color reversal process such as the Kodak E-6™ process. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

[0088] The above emulsions are typically sold with instructions to process using the appropriate method such as the mentioned color negative (Kodak C-41) or reversal (Kodak E-6) process.

[0089] Preferred color developing agents are *p*-phenylenediamines such as:

4-amino-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline sesquisulfate hydrate,
4-amino-3 -methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate,
4-amino-3-(2-methanesulfonamidoethyl)-N,N-diethylaniline hydrochloride, and
4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-*p*-toluene sulfonic acid.

[0090] Of the above, developers based on 4-amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline and 4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline are especially preferred. Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

Synthesis Example

Synthesis of 6-(tetradecyloxy)purine (A):

[0091] Potassium *tert*-butoxide (284.50g, 2.54mol) was added to a stirred solution of tetradecanol (271.75g, 1.27mol) in tetrahydrofuran (5l) under an atmosphere of nitrogen. A thick precipitate formed and the reaction became slightly warm. The reaction was stirred for 0.5 h and then 6-chloropurine (196.20g, 1.27mol) was added and the reaction stirred for 0.25 h before being heated at reflux for 3 h. The reaction was allowed to cool, and then the solvent was removed *in vacuo*. First water (4 l) then concentrated hydrochloric acid (135 ml, 1.35mol) was added to the residue and the suspension was stirred for 0.5 h after which time it was still acidic. The suspension was neutralized with saturated sodium hydrogen carbonate solution. After stirring vigorously for 0.5 h the solid was removed by filtration and recrystallized from methanol (about 4.5 l). A small amount of solid did not dissolve. The suspension was allowed to cool to room temperature but was not cooled further. This gave a white solid that was recrystallized once more from methanol (about 4.5 l). Again, a small amount of solid did not dissolve so it was removed whilst the methanol was still hot. This solid was insoluble in water and common organic solvents (acetone, methanol, tetrahydrofuran, ethyl acetate and dichloromethane). The suspension was allowed to cool to room temperature. Filtration and drying at oil pump vacuum (approximately 300 ml of methanol removed) gave a white solid (325.90g).

Emulsion and Photographic Examples.

[0092] Formulas for the compounds not previously identified are provided following the examples. The examples illustrate the practice of this invention. They are not intended to be exhaustive of all possible variations of the invention. Parts and percentages are by weight unless otherwise indicated.

[0093] The following emulsion examples were optimally sulfur and gold sensitized with the a rapid sulfiding compound S1 disclosed in U.S. Patent 4,810,626 (Burmaier) and the gold (I) compound A1 disclosed in U.S. Patent 5,049,485 (Deaton). The emulsion was spectrally sensitized with a combination of GSD-1 and GSD-2 as green sensitizer dyes present during the sensitization.

[0094] *Emulsion A:* A 1.7 x 0.12 μm silver bromoiodide (overall iodide content 4.5%) tabular grain emulsion was prepared by the following method: To a 4.6 liter aqueous solution containing 0.4 weight % bone gelatin and 7 g/L sodium bromide at 51.5°C with vigorous stirring in the reaction vessel was added by single jet addition of 0.42M silver nitrate solution at constant flow rate over a 15-minute period, consuming 1.8% of total silver. Subsequently, 23.1 g of ammonium sulfate was added to the vessel, followed by the addition of 100 mL sodium hydroxide at 2.3M. After 5 min, 142 mL nitric acid at 2.5M was added. Then 3 liters of aqueous solution containing 0.74% gelatin by weight and 11.3 g of sodium bromide at 51.5°C were added to the reaction vessel and held for 5 minutes. Then double jet addition of an aqueous 3.0M silver nitrate solution and an aqueous solution of 3.0M sodium bromide were added simultaneously to the reaction vessel utilizing accelerated flow rate (21.3X from start to finish) over 46 minutes while controlling pBr at 1.7, consuming 67 mole % of total silver. At 44 minute into this segment, a 70 mL of aqueous solution of potassium hexacyanoruthenate at 0.35% by weight was then added to the reaction vessel. Both silver and salt solutions were halted after the accelerated flow segment while the pBr of the vessel was adjusted to 1.1 by addition of sodium bromide salt. Then 130 mL of an aqueous solution of potassium selenocyanate at 4% by weight was added to the reaction vessel. Silver iodide Lippmann seed at 4.5 mole % of total silver was then added to the reaction vessel. After a two-minute period halt, the 3.0M silver nitrate solution was used to adjust the pBr from 1.1 to 2.5. Then the 3.0M sodium bromide solution was added simultaneously with the silver nitrate solution to the reaction vessel to control pBr at 2.5 until a total of 12.6 mole silver was prepared. The emulsion was cooled to 40°C and washed by ultrafiltration method.

[0095] *Example A1M:* Each mole of Emulsion A was optimally sensitized with 0.93 mmoles of sodium thiocyanate, 0.09 mmoles of F1, 0.76 mmole of GSD-2 and 0.19 mmole of GSD-1 green sensitizing dyes, and with 2.29 mg of sulfur sensitizer S1 and 2.2 mg of gold sensitizer A1. The emulsion was then subjected to a fourteen minute heat digest at 60°C and chill set.

[0096] *Example A2M:* Each mole of Emulsion A was optimally sensitized with 0.93 mmoles of sodium thiocyanate, 43 μmole of compound A added as a 3% dispersion in solvent CS1, 0.09 mmoles of F1, 0.76 mmole of GSD-2 and 0.19 mmole of GSD-1 green sensitizing dyes, and with 2.29 mg of sulfur sensitizer S1 and 2.2 mg of gold sensitizer A1. The emulsion was then subjected to a fourteen minute heat digest at 60°C and chill set.

[0097] *Example A3M*: Each mole of Emulsion A was optimally sensitized with 0.93 mmoles of sodium thiocyanate, 40 μmole of compound X added as a 3% dispersion in solvent CS1, 0.09 mmoles of F1, 0.76 mmole of GSD-2 and

0.19 mmole of GSD-1 green sensitizing dyes, and with 2.29 mg of sulfur sensitizer S1 and 2.2 mg of gold sensitizer A1. The emulsion was then subjected to a fourteen minute heat digest at 60°C and chill set.

[0098] *Example A4M:* Each mole of Emulsion A was optimally sensitized with 0.93 mmoles of sodium thiocyanate, 40 μmole of compound X added from a methanol solution, 0.09 mmoles of F1, 0.76 mmole of GSD-2 and 0.19 mmole of GSD-1 green sensitizing dyes, and with 2.29 mg of sulfur sensitizer S1 and 2.2 mg of gold sensitizer A1. The emulsion was then subjected to a fourteen minute heat digest at 60°C and chill set.

[0099] Single layer coatings on a transparent film support were prepared using a silver coverage of 0.81 g/m^2, magenta dye forming coupler at a coverage of 0.22 g/m^2 of M-1.

[0100] Samples of the coatings were exposed by a daylight balanced tungsten light source through a graduated density test object and a Wratten 9 filter (wavelength > 480 nm transmitted) for magenta records. Processing was conducted using the Kodak Flexicolor™ C-41 color negative processing chemicals and procedures. The sensitometric speed comparisons are made with the minimum density (fog) and the relative speed at an optical density of 0.15 above the minimum density. Each speed unit difference is equal to 0.01 logE, where E represents the light exposure in lux-seconds unit.

[0101] Granularity readings on the same processed strips were made according to procedures described in the *SPSE Handbook of Photographic Science and Engineering,* edited by W. Thomas, pp. 934-939. Granularity readings at each step were divided by the contrast at the same step, and the minimum contrast normalized granularity reading was recorded. Contrast normalized granularity is reported in grain units (g.u.), in which each g.u. represents a 5% change. A positive change corresponds to a grainier image, and negative changes are desirable. Since the random dot model for granularity predicts that granularity is inversely proportional to the square root of the number of imaging centers (M.A. Kriss in *The Theory of the Photographic Process,* 4th Ed. T. H. James, ed. New York, Macmillan, 1977; p.625), and larger grains generally are needed to achieve higher speeds, it is typical that, for tabular emulsions, granularity will increase at a rate of ca. 7 g.u. for each gain of 30 log speed units (ratio of 1/7.5) at constant silver coverage and photoefficiency. Results are shown in Table 1.

TABLE 1 -

Color Process			
Speed, Fog, and Contrast Normalized Granularity Responses			
Example	Fog (Dmin)	Relative Speed (log units)	Relative. Granularity (g.u.).
A1M	0.147	Check	Check
A2M	0.107	-3	-2.5
A3M	0.118	0	-1.0
A4M	0.095	-4	-1.5

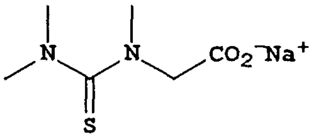
[0102] The data in Table 1 clearly demonstrates that the addition of the antifogging compound useful in the invention significantly lowers fog and improves granularity with a modest loss in speed.

[0103] In order to demonstrate utility in a black-and-white (non-color forming) process, examples A1M and A3M were additionally exposed as above and processed in the KODAK™ Rapid X-Ray Developer Process using KRX black and white developer. The results shown in Table 2 clearly indicate that the compounds also serve to reduce Dmin and improve granularity while increasing speed in a black-and-white process.

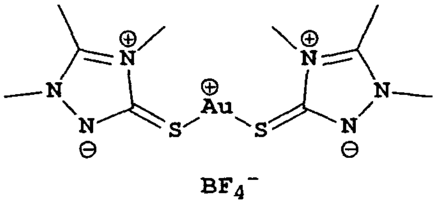
TABLE 2 -

Black-and-White Process			
Speed, Fog, and Contrast Normalized Granularity Responses			
Example	Fog (Dmin)	Relative Speed (log units)	Relative. Granularity (g.u.).
A1M	0.072	Check	Check
A3M	0.067	+3	-1.0

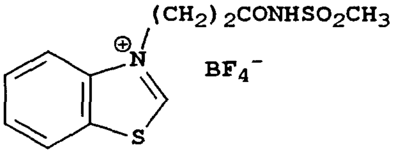
S1:



A1:



F1:



CS1: N,N-Dibutyllauramide

Claims

1. A photographic element comprising a layer containing a silver halide emulsion chemically or spectrally sensitized or both in the presence a heterocycle compound with a minimum of three heteroatoms that does not react with oxidized developer and has a ClogP greater or equal to 6.2.

2. The photographic element of claim 1 wherein the ratio of the number of millimoles of the heterocycle compound to the number of moles of silver in the same layer is less than 1.0.

3. The photographic element of claim 1 wherein the ratio of the number of millimoles of the heterocycle compound to the number of moles of silver in the same layer is less than 0.1.

4. The photographic element of claim 1 wherein the heterocycle compound is added to the silver halide emulsion prior to or concurrent with spectral sensitization.

5. The photographic element of claim 7 in which the emulsion further comprises a thiourea sensitizer.

6. The photographic element of claim 4 wherein the emulsion further comprises a gold sensitizer.

7. The photographic element of claim 1 wherein the heterocycle compound is added to the silver halide emulsion prior to or concurrent with a chemical sensitization step but prior to a digest step, if any, using a temperature increase of at least 5°C.

8. The photographic element of claim 1 wherein the heterocycle compound is dispersed in a hydrophobic organic solvent.

9. The photographic element of claim 8 wherein the hydrophobic organic solvent has a ClogP of 5.0 or greater and a *beta* of 0.4 or more.

10. The photographic element of claim 1 wherein the heterocycle compound is dispersed as a finely ground solid particle state.

11. The photographic element of claim 1 wherein the heterocycle compound is a nitrogen heterocycle containing at least two fused rings.

12. The photographic element of claim 1 wherein the heterocycle compound is a 1,3,4,6-tetraazaindene (purine).