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(54) **Density correction dyes for color negative films with magnetic recording layers**

(57) The invention provides a multilayer color negative photographic element comprising a support, at least one light-sensitive silver halide emulsion layer sensitive to each of the blue, green and red regions of the visible spectrum, a magnetic recording layer, and a permanent density correction dye, wherein:

the spectral absorbance maximum of the density correction dye is in the range of 450-485 nm;
the ratio of the absorbance of the density correction dye at 480 nm relative to 420 nm is between 1.2 and 3.5;

the ratio of the absorbance of the density correction dye at 440 nm relative to 420 nm is between 1.25 and 2.5;

the ratio of the absorbance of the density correction dye at 510 nm relative to 480 nm is less than 0.6;
and

the density correction dye is uncharged and is free of carboxyl and sulfonate groups.

The element exhibits improved color balance permitting it to be satisfactorily processed together with conventional photographic elements to produce viewable color images.

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DescriptionField of the Invention

5 This invention relates to color negative photographic materials or elements comprising yellow density correction dyes and transparent magnetic recording layers.

Background of the Invention

10 Modern color negative films usually contain dyes coated in one or more layers for a variety of purposes. In addition to being utilized for spectral sensitization, dyes may be used for filtration of specific wavelengths of exposing light (either as intergrain absorbers or in separate layers containing no silver halide), for antihalation and to adjust the background density (Dmin) of color negative films for printing purposes. Dyes that are used to adjust Dmin of color negative films to produce prints of proper color balance may be referred to as density correction dyes. However, such
15 dyes may also be used for filtration and/or antihalation purposes.

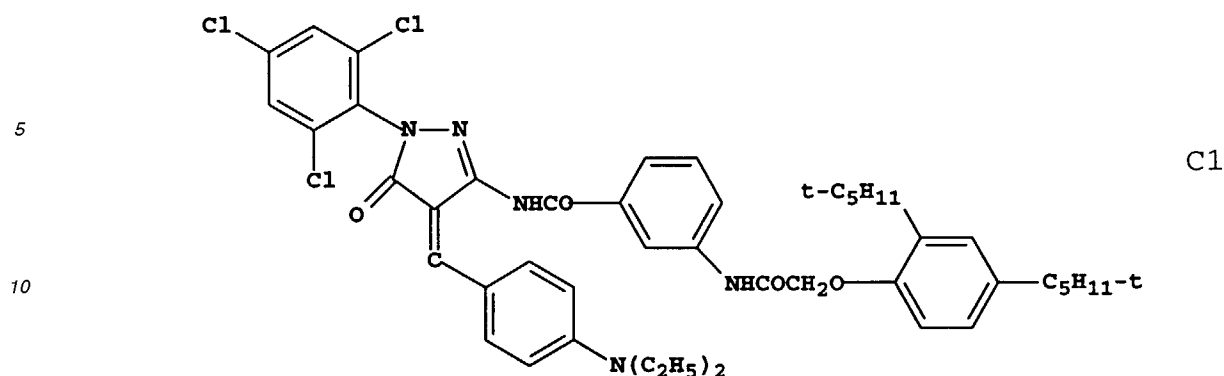
A recent advance in the structure of color negative films comprises use of magnetic recording layers to encode useful information for printing and other purposes. The magnetic recording layers can contain magnetic particles of a variety of types, sizes and shapes, but are generally designed to be transparent to visible light. Additional descriptions of such magnetic layers may be found, for example, in Research Disclosure, November 1992, Item 34390, p 869 and
20 in U.S. Patent 5,395,743 of Brick et al. Although, the magnetic recording layers are essentially transparent, the magnetic particles and/or the polymeric supports used for color negative films with magnetic recording layers can lead to higher absorption in the far blue region of the visible spectrum (ca 400-440 nm) than is typical for conventional color negative films. The differences in the far blue absorption of conventional films and films containing magnetic recording layers can lead to differences in print color balance when these films are printed together on certain printers.

25 Many color printers scan the average red, green and blue densities of a color negative and use these readings to automatically adjust exposures for proper density and color balance. The spectral sensitivities of printer scanners often do not match the spectral sensitivities of color papers. While most color papers have peak blue sensitivities in the neighborhood of 480 nm and little sensitivity in the far blue region, some printers, such as the AGFA MSP printer, have considerable blue sensitivity in the region of 400 to 440 nm. When two color negative films having different density
30 ratios at 480 nm vs 400-440 nm are printed together using a printer such as the AGFA MSP, the resulting prints will have different color balance, and the two films are said to be printer incompatible. Since a printer such as the AGFA MSP printer may see different blue densities for a conventional color negative film and a film with a magnetic recording layer, even if the films have the same blue densities in the region of color paper sensitivity, it may expose such films differently leading to unacceptable differences in color balance.

35 One approach for avoiding color balance problems and maintaining printer compatibility for films containing magnetic recording layers is to incorporate one or more density correction dyes that spectrally compensate for the differences in the far blue absorption of the magnetic film and conventional color negative films. Since films containing magnetic recording layers generally have greater far blue absorption than conventional films, this compensation is most suitably achieved by replacing conventional yellow or orange density correction dyes with one or more yellow
40 dyes having reduced absorption in the region of approximately 400-440 nm. Since some conventional color negative films also contain orange color correction dyes, such as C1 below, that absorb strongly in the region of 480 nm, it may also be desirable to select a single yellow density correction dye with both less absorption in the 400-440 nm region and greater absorption near 480 nm to replace both the conventional yellow and orange density correction dyes. In addition to having these spectral properties, it is desired that the yellow density correction dyes utilized in color negative
45 films with magnetic recording layers be inexpensive, readily dispersible and stable toward heat, moisture and photographic processing chemicals.

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There is now a considerable body of art relating to the magnetic recording layers. In addition to the above noted U.S. 5,395,743 and Research Disclosure, November 1992, Item 34390 the following U.S. Patents may be relevant: 4,141,735, 4,990,276, 5,147,768, 5,217,804, 5,229,259, 5,252,441, 5,294,437, 5,368,997 and 5,395,743. These patents do not recognize the printing problem created by the addition of a magnetic layer to the film structure.

Accordingly, a problem to be solved is to provide a color negative photographic element containing a magnetic layer, which is capable of being processed at the same time as conventional films which do not contain a magnetic layer, without introducing a yellow coloration into the prints produced from the magnetic layer containing film.

Summary of the Invention

The invention provides a multilayer color negative photographic element comprising a support, at least one light-sensitive silver halide emulsion layer sensitive to each of the blue, green and red regions of the visible spectrum, a magnetic recording layer, and a permanent density correction dye, wherein:

- the spectral absorbance maximum of the density correction dye is in the range of 450-485 nm;
- the ratio of the absorbance of the density correction dye at 480 nm relative to 420 nm is between 1.2 and 3.5;
- the ratio of the absorbance of the density correction dye at 440 nm relative to 420 nm is between 1.25 and 2.5;
- the ratio of the absorbance of the density correction dye at 510 nm relative to 480 nm is less than 0.6; and
- the density correction dye is uncharged and is free of carboxyl and sulfonate groups.

The element exhibits improved color balance permitting it to be satisfactorily processed together with conventional photographic elements to produce viewable color images which do not have undesired yellow coloration in some printers.

Detailed Description of the Invention

This invention relates to color negative photographic materials or elements comprising one or more yellow or orange-yellow density correction dyes having the spectral properties described in the SUMMARY OF THE INVENTION and one or more magnetic recording layer(s). The density correction dyes of the invention may also function as filter dyes and/or antihalation dyes and may be coated in various layers including a filtration layer between blue and green sensitive layers and in an antihalation layer under (further from the exposing light) the light sensitive silver halide layers.

The invention provides color negative films with magnetic recording layers that provide viewable media such as prints having the proper color balance when printed together with conventional (nonmagnetic) color negative films. This means that separate settings or separate processing for the film having the magnetic layer is not required in order to obtain satisfactory prints. The invention also provides thinner color negative films with reduced chemical laydown through the use of high extinction density correction dyes of the proper hue. Further, the density correction dyes of the invention may also serve as filter dyes or antihalation dyes. Moreover, the density correction dyes are easily and inexpensively manufactured and readily dispersible.

To ensure that the density correction dyes of this invention are permanent, i.e. do not wash out or bleach on processing, the log P of the dye (calculated by the program Medchem, version 3.54, as described in "Exploring QSAR", C. Hansch and A. Leo, American Chemical Society, Washington, D.C. 1995) should be at least 4.0 and preferably 5.0 or greater.

Suitably, for the coated density correction dyes of this invention the absorbance maximum is between 455 and

480 nm, the ratio of absorbance at 480 nm relative to 420 nm is between 1.3 and 3.0, the ratio of absorbance at 440 nm relative to 420 nm is between 1.35 and 2.2 and the ratio of absorbance at 510 nm relative to 480 nm is less than or equal to 0.55. These absorbances are determined for the dyes in their "as coated" states.

Useful coated levels of the density correction dyes of this invention depend upon molecular weight and extinction coefficient, but typically range from 0.005 to 0.16 g/sq m, with levels of 0.011 to 0.11 g/sq m being more typical.

The density correction dyes of this invention may, for example, be incorporated in the photographic materials by first dispersing a dye-containing oil phase in an aqueous phase containing a binder, such as gelatin, and one or more surfactants. The dye-containing dispersion is then coated in the appropriate layer of a multilayer film on a suitable support. The oil phase usually consists of the dye dissolved in one or more high-boiling solvents. This is typically added to an aqueous solution of gelatin and surfactant, which is followed by milling or homogenization of the mixture to disperse the oil phase in the aqueous phase as small particles. Auxiliary solvents (removable by washing or evaporation) such as ethyl acetate or cyclohexanone may also be used in the preparation of such dispersions to facilitate dissolution of the dye in the oil phase. However, some yellow dyes of this invention do not require the use of a removable auxiliary solvent for dispersion preparation. The yellow dyes of this invention may also be dispersed as solid particle dispersions via ball milling.

Hues of the density correction dyes of this invention can be shifted to optimize the spectral properties by choice of high-boiling solvent. High-boiling solvents useful for the practice of this invention include aryl phosphates (e.g. tricresyl phosphate), alkyl phosphates (e.g. trioctyl phosphate), mixed aryl alkyl phosphates (e.g. diphenyl 2-ethylhexyl phosphate), aryl, alkyl or mixed aryl-alkyl phosphonates, phosphine oxides (e.g. trioctylphosphine oxide), esters of aromatic acids (e.g. dibutyl phthalate), esters of aliphatic acids (e.g. dibutyl sebacate), alcohols (e.g. 2-hexyl-1-decanol), phenols (e.g. p-dodecylphenol), carbonamides (e.g. N,N-dibutyldodecanamide or N-butylacetanilide), sulfoxides (e.g. bis(2-ethylhexyl)sulfoxide), sulfonamides (e.g. N,N-dibutyl-p-toluenesulfonamide) or hydrocarbons (e.g. dodecylbenzene). Additional high-boiling solvents and auxiliary solvents are noted in Research Disclosure, December 1989, Item 308119, p 993. Useful dye:high-boiling solvent weight ratios range from about 1:0.1 to 1:10, with 1:0.2 to 1:5.0 being typical. The yellow dyes of this invention may also be dispersed without the use of a permanent high-boiling solvent.

The color negative films of this invention can comprise one or more transparent magnetic recording layers, comprising ferromagnetic particles having a size of at least 20 sq m/g and coated at a level of from 1x10⁴ to 2x10⁵ g/m³. The ferromagnetic particles comprise iron oxides such as gamma-Fe₂O₃, Fe₃O₄, or iron oxides such as gamma-Fe₂O₃ or Fe₃O₄ surface treated with Co, Zn, Ni or other metals. The ferromagnetic particles of this invention also comprise chromium dioxides, such as CrO₂ or CrO₂ with metallic elements such as Li, Na, Sn, Pb, Fe, Co, Ni or Zn in solid solution. The ferromagnetic particles of this invention may also comprise barium ferrites. Ferromagnetic metal particles with a surface oxide coating to improve stability may also be used in accordance with this invention. In addition magnetic oxides with a thicker layer of lower refractive oxide or other material having a lower optical scattering cross-section, as taught in U.S. 5,217,804 and 5,252,444, may also be used. Cobalt surface-treated gamma iron oxide is a very suitable ferromagnetic recording material for use in accordance with this invention.

On an area basis, useful coated magnetic particle concentrations are between about 0.01 and 0.25 g/sq m, with a range of 0.02 to 0.08 g/sq m being typical for the color negative films of this invention.

The magnetic layer(s) of this invention may also contain abrasive particles comprising nonmagnetic inorganic powders with a Mohs scale hardness of at least 6. Specific examples include, aluminum oxides (such as alpha alumina), tin oxides, Cr₂O₃, alpha-Fe₂O₃, silicon dioxide, titanium dioxide and silicon carbide. Alpha alumina, tin oxides and mixtures thereof are the preferred abrasives. The tin oxides may be undoped or doped and in the nonconductive or conductive forms.

A wide variety of binders may be used in the magnetic recording layers of this invention, including polyurethane resins and cellulose derivatives. Cellulose esters, such as cellulose acetate, cellulose diacetate, cellulose triacetate, cellulose acetate propionate and cellulose acetate butyrate are particularly preferred binders. Mixtures of cellulose diacetate and cellulose triacetate serve as particularly useful binders in the magnetic recording layers of this invention.

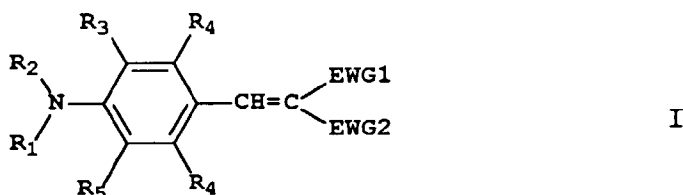
The photographic materials of this invention can be provided with a protective or lubricating layer comprising materials such as silicone oil or carnauba wax over the magnetic recording layer.

Any suitable photographic film support may be employed in the practice of this invention, such as cellulose derivatives (including cellulose diacetate, cellulose triacetate, cellulose acetate propionate and cellulose acetate butyrate), polyamides, polycarbonates, polyesters (such as polyethylene terephthalate and polyethylene naphthalate), polystyrene, polyethylene and polypropylene. Suitable exemplary supports for the practice of this invention are polyethylene naphthalate, polyethylene terephthalate and cellulose triacetate.

The yellow density correction dyes of this invention may be coated in the color negative photographic materials of this invention either alone in one or more layers or together with other dyes or addenda in the same layers or layer. The yellow dyes of this invention can be coated in any layer on either side of the support. In one embodiment of this invention, the yellow density correction dyes are coated in an antihalation layer under (i.e. furthest from the direction

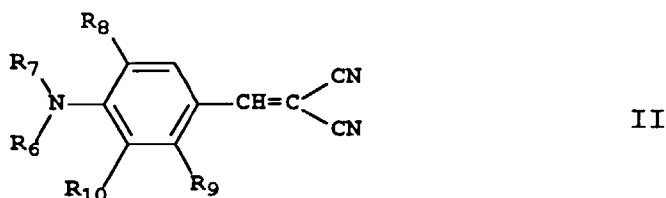
of exposure) the light-sensitive silver halide layers. The antihalation layer is often adjacent to a transparent support. The yellow dyes of this invention may also be coated between the green-sensitive and red-sensitive layers of the color negative films of this invention. In another embodiment, the yellow dyes of this invention are coated in a filtration layer under the blue-sensitive layer(s) and over the green sensitive layer(s) of the color negative film. This reduces unwanted blue exposure of the green-sensitive layers and can allow elimination of some or all of normally used filtration materials, such as bleachable yellow dyes or Carey-Lea silver thus enabling layer thinning. The yellow dyes of this invention may also be coated above the blue sensitive layer(s) of the color negative films for adjustment of blue speed. The yellow dyes of this invention may also be coated in an emulsion-containing layer such as the least-sensitive magenta dye forming layer.

One useful embodiment of this invention comprises yellow or orange-yellow arylidine methine-type density correction dyes of structure I, or II below



wherein:

- R1 is hydrogen or an alkyl group;
- R2 is an alkyl group or an aryl group;
- R3 is hydrogen, an alkyl group, an alkoxy group or an aryloxy group;
- R4 is hydrogen, an alkyl group or an alkoxy group;
- R5 is hydrogen or an alkyl group ;
- R1 and R2, R2 and R3 or R1 and R5 may join to form a ring ; and
- EWG1 and EWG2 are electron-withdrawing groups.



wherein:

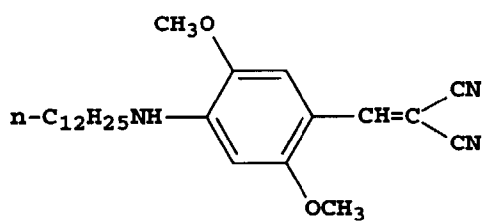
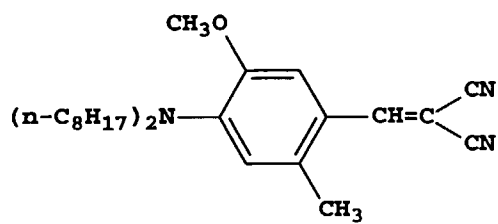
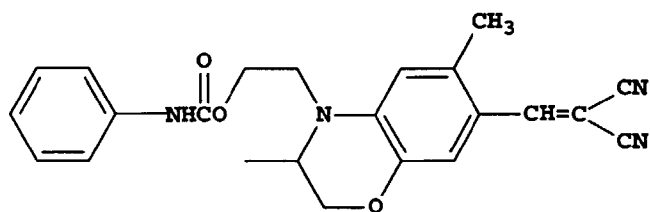
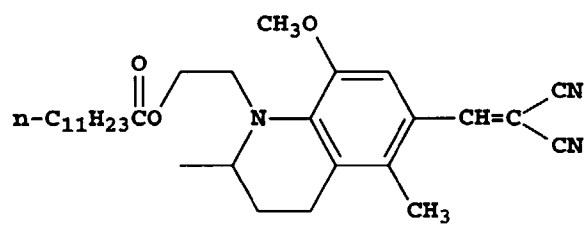
- R6 is an alkyl group;
- R7 is an alkyl group or an aryl group;
- R8 is an alkyl group, an alkoxy group or an aryloxy group;
- R9 is an alkyl group or an alkoxy group;
- R10 is hydrogen or an alkyl group;
- R6 and R7, R7 and R8 or R6 and R10 may join to form a ring; and
- the total number of carbon atoms in R6-R10 taken together is at least 12.

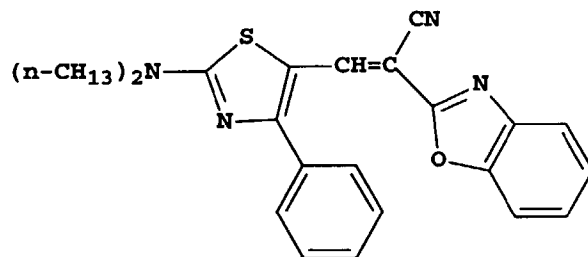
In another embodiment of this invention the density correction dye is of structure II, R6, R7 and R9 are alkyl groups and R8 is an alkoxy group.

The alkyl groups of R1-R10 may be straight chain, branched or cyclic and may be unsubstituted or substituted with any group that does not adversely affect the performance of the invention. The aryl groups of R2 or R7, the alkoxy groups of R3, R4, R8 or R9, and the aryloxy groups of R3 or R8 may also be unsubstituted or substituted with any group that does not adversely affect the performance of the invention. An alkoxy group of R3 may form a ring with the alkyl group of R2 or the alkoxy group of R8 may form a ring with the alkyl group of R7.

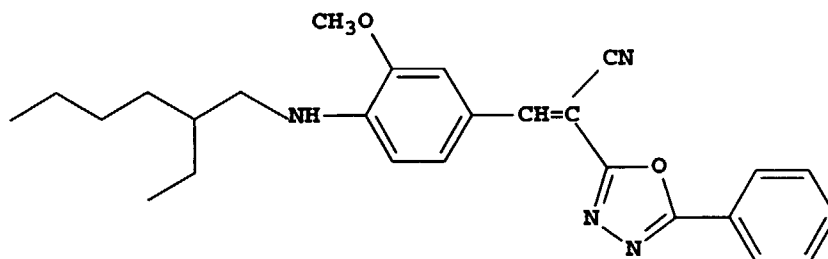
Examples of yellow methine density correction dyes of this invention include, but are not limited to, the following

(D1-D26):

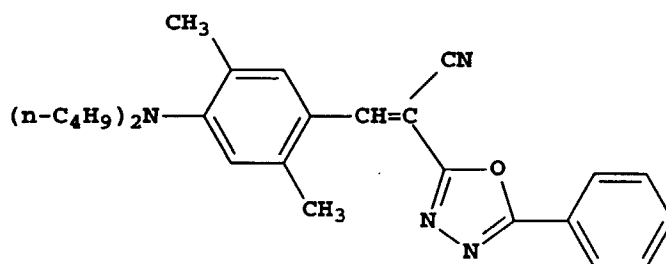




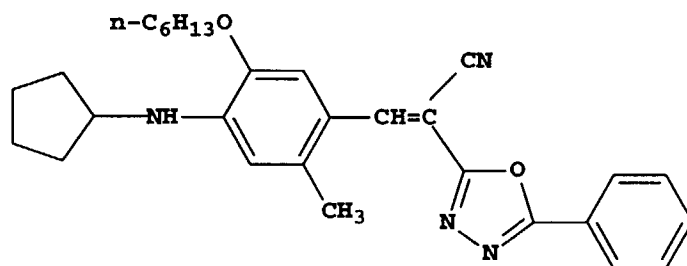
D5



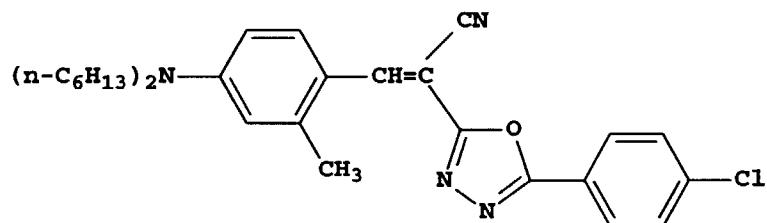
D6



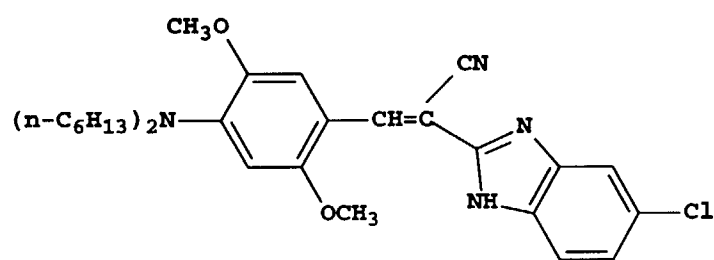
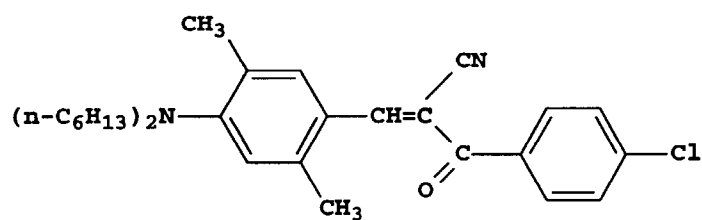
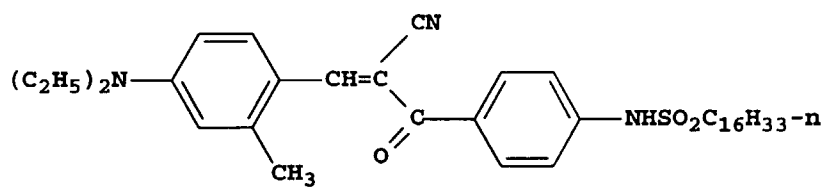
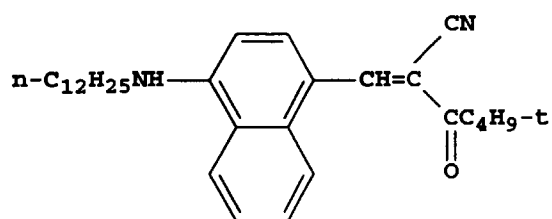
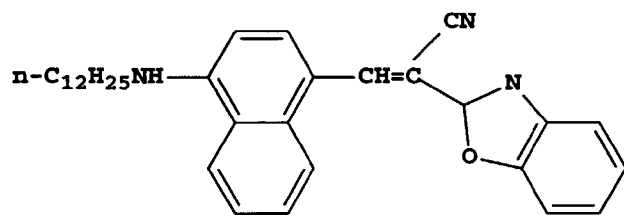
D7

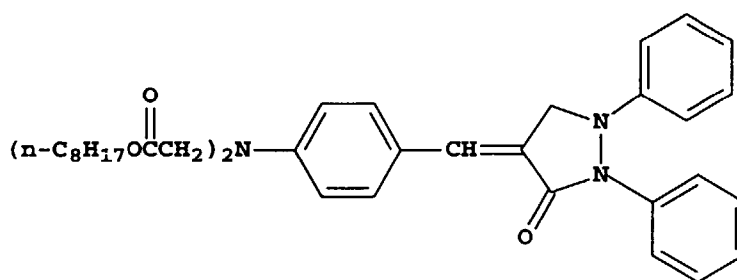
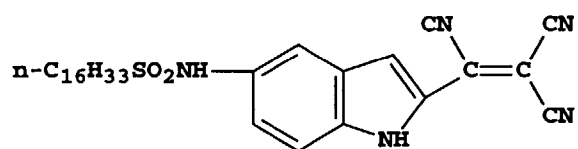
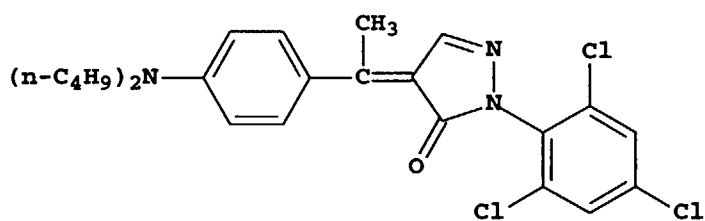
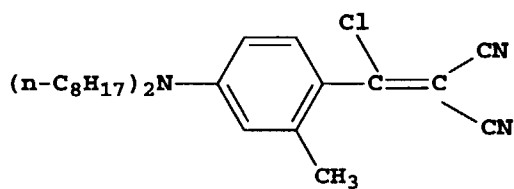
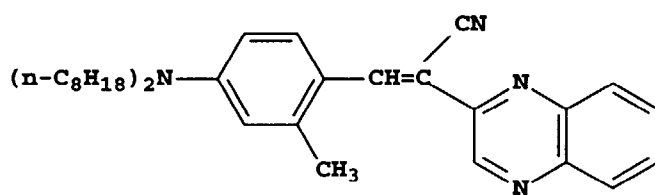


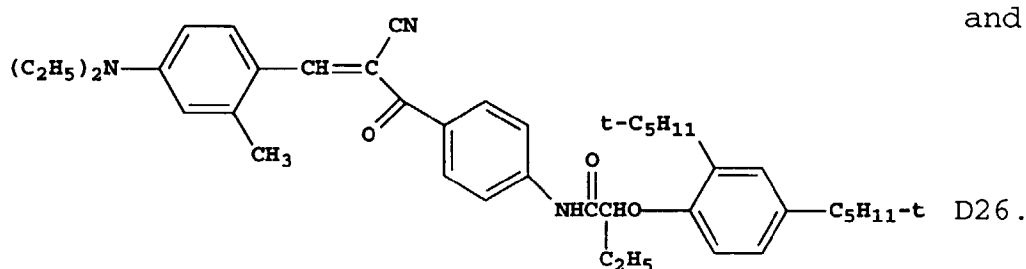
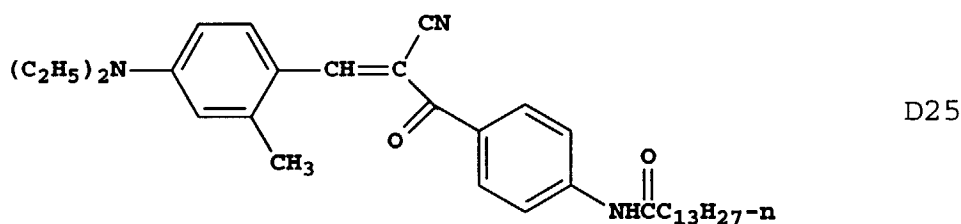
D8



D9

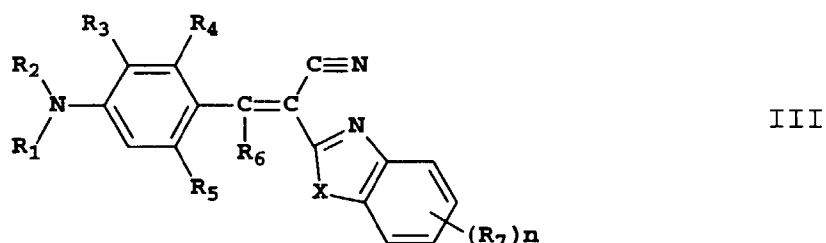






Embodiment A

In one preferred embodiment, a multilayer color negative photographic element comprising a support, at least one light-sensitive silver halide layer sensitive to each of the blue, green and red regions of the visible spectrum, a magnetic recording layer and a yellow or orange-yellow methine density correction dye of structure III,



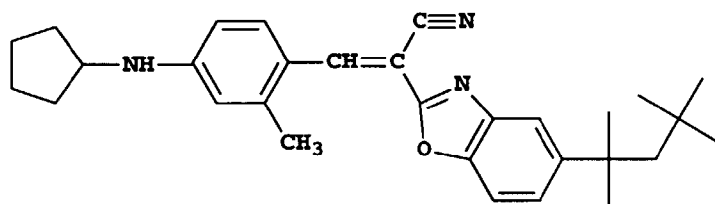
wherein:

- R_1 is hydrogen or an alkyl group;
- R_2 is an alkyl group or an aryl group;
- R_3 is hydrogen, a halogen atom, an alkyl group, an alkoxy group or an aryloxy group;
- R_4 is hydrogen or an alkyl group;
- R_5 is hydrogen or an alkyl group;
- R_6 is hydrogen or an alkyl group;
- X is oxygen or sulfur;
- each R_7 is independently a substituent selected from the group consisting of a halogen atom, and alkyl, aryl, alkoxy, aryloxy, carbonamido, sulfonamido, carbamoyl, alkoxycarbonyl, aryloxycarbonyl, acyloxy, acyl, sulfamoyl, sulfonyl, sulfoxyl, alkylthio, arylthio and cyano groups;
- n is 0, 1, 2 or 3; and
- R_1 and R_2 or R_2 and R_3 may join to form a ring.

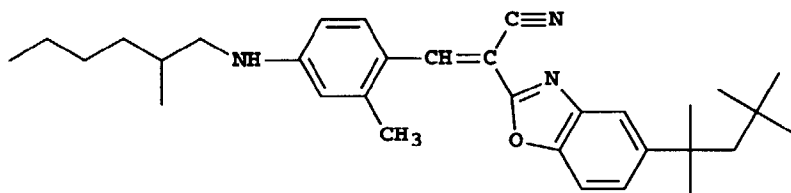
In one form of this invention R₁ is hydrogen. In another embodiment of this invention R₂ is an alkyl group. In another form of this invention n is 0, 1 or 2. In a preferred form of this embodiment of this invention R₄ is hydrogen. In another preferred form X is oxygen. In another form R₅ is an alkyl group. In another form R₃ is an alkoxy group. In another form R₆ is hydrogen. In a particularly suitable embodiment of this invention R₁ is hydrogen, R₂ is alkyl, R₃ is hydrogen or alkyl, R₄ is hydrogen, R₅ is alkyl, R₆ is hydrogen, X is oxygen, n is 0 or 1, and R₇ is an alkyl group, a sulfonamido group or a halogen atom, such as chlorine, in the para position relative to the oxygen of the benzofuran ring. In another particularly suitable embodiment of this invention R₁ and R₂ are alkyl groups, R₃, R₄ and R₆ are hydrogen, R₅ is an alkyl group, n is 0 or 1 and R₇ is an alkyl group, a sulfonamido group or a halogen in the para position relative to X, which is oxygen.

The alkyl substituents comprising R₁ through R₇ may be unbranched, branched or cyclic and may be unsubstituted or substituted. The alkoxy groups comprising R₃ or R₇ may be unbranched or branched and may be substituted or unsubstituted. The aryl groups comprising R₂ or R₇ and the aryloxy groups comprising R₃ or R₇ may be unsubstituted or substituted. The carbonamido, sulfonamido, carbamoyl, acyloxy, alkoxycarbonyl and aryloxy carbonyl, acyl, sulfamoyl, sulfonyl, sulfoxyl, alkylthio and arylthio groups comprising R₇ may also be further substituted. Any substituent may be chosen for the alkyl, aryl, alkoxy, aryloxy and R₇ groups that does not adversely affect the performance of the yellow methine density correction dyes of this invention. Suitable substituents include halogen atoms, such as chlorine, alkenyl groups, alkynyl groups, aryl groups, hydroxy groups, alkoxy groups, aryloxy groups, acyl groups, acyloxy groups, alkoxycarbonyl groups, aryloxy carbonyl groups, carbonamido groups (including alkyl-, aryl-, alkoxy-, aryloxy- and alkylamino-carbonamido groups), carbamoyl groups, carbamoyloxy groups, sulfonamido groups, sulfamoyl groups, alkylthio groups, arylthio groups, sulfoxide groups, sulfonyl groups, sulfonyloxy groups, alkoxysulfonyl groups, aryloxysulfonyl groups, trifluoromethyl groups, cyano groups, imido groups and heterocyclic groups, such as 2-furyl, 3-furyl, 2-thienyl, 1-pyrrolyl, 2-pyrrolyl, 1-imidazolyl and N-succinimidyl groups. The aryl groups comprising R₂ and the groups comprising R₇ may also be substituted with one or more unbranched, branched or cyclic alkyl groups.

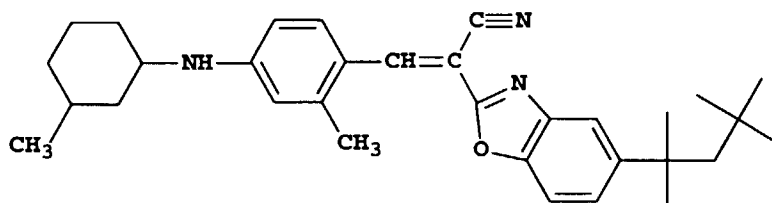
Examples of nondiffusible yellow methine density correction dyes of this preferred embodiment A include, but are not limited to, the following (DA1-DA35) :



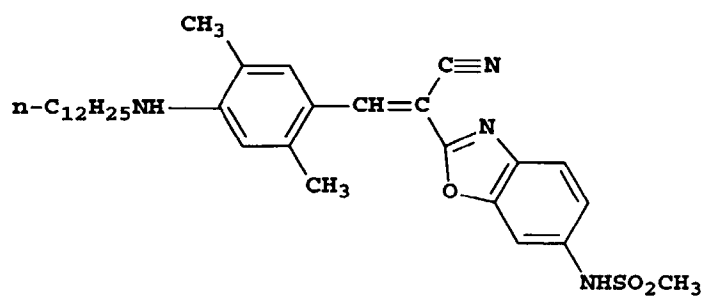
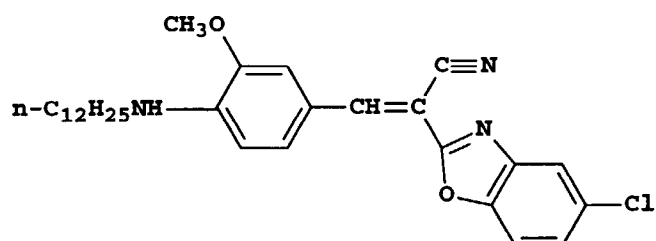
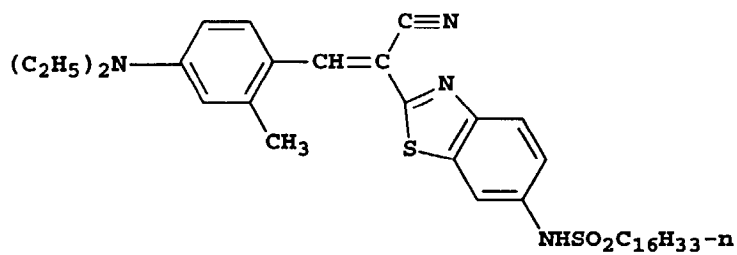
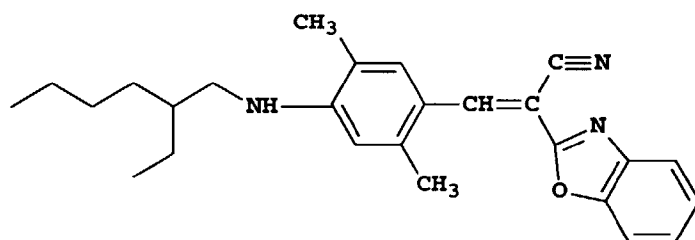
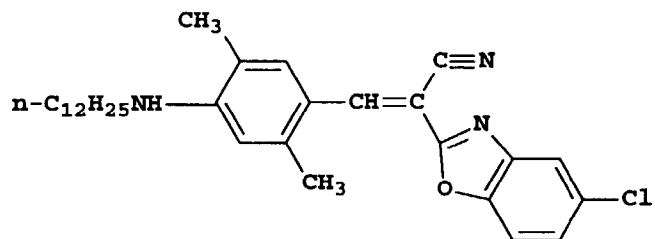
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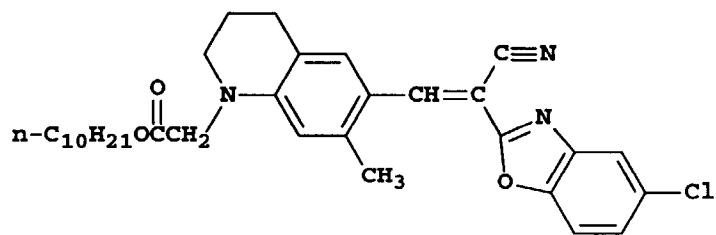


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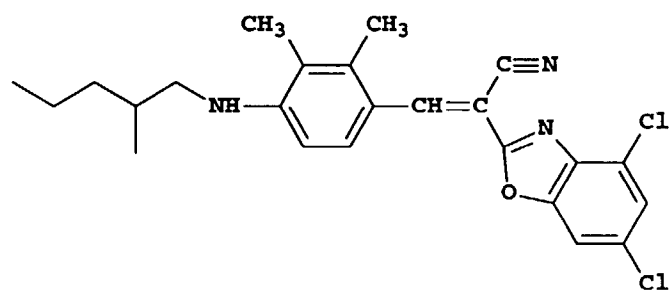


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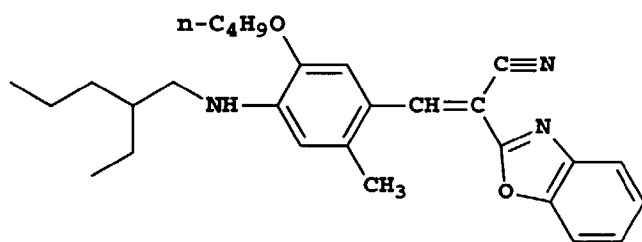




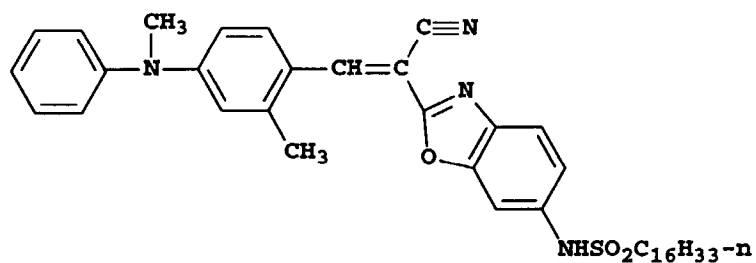
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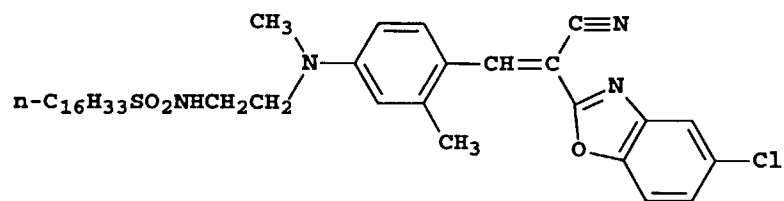
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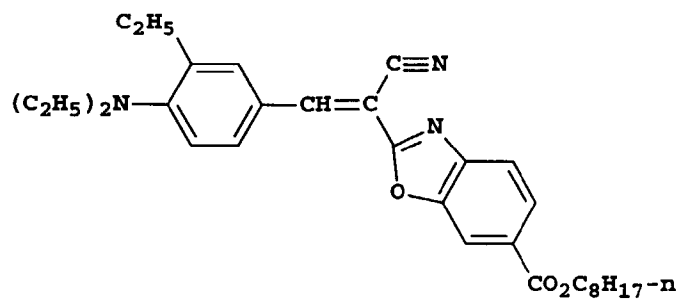
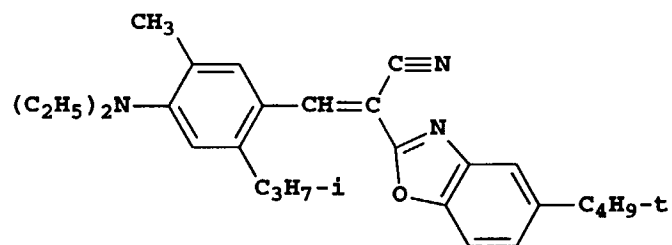
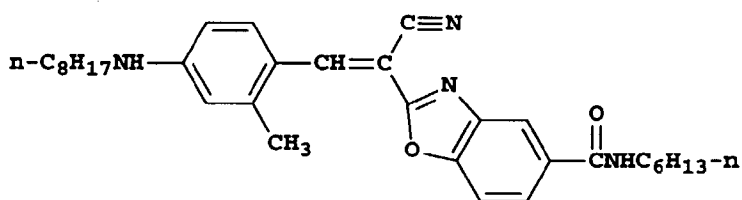
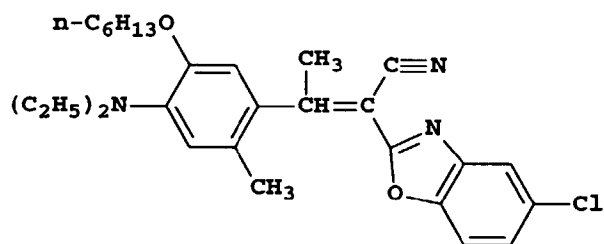
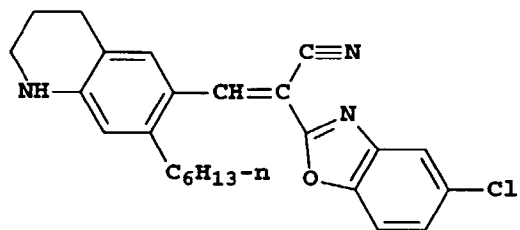
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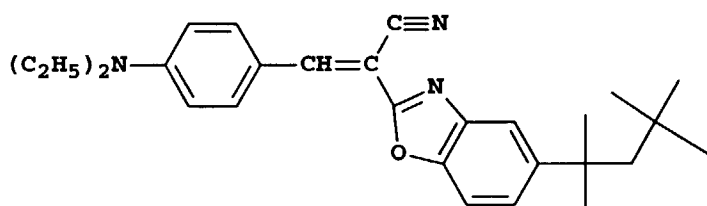
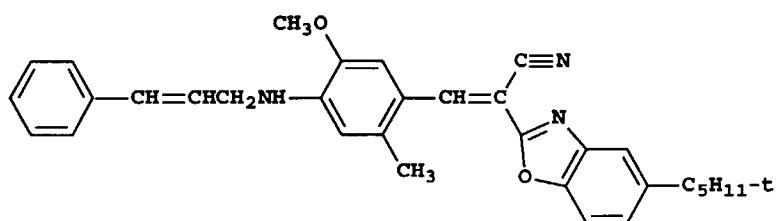
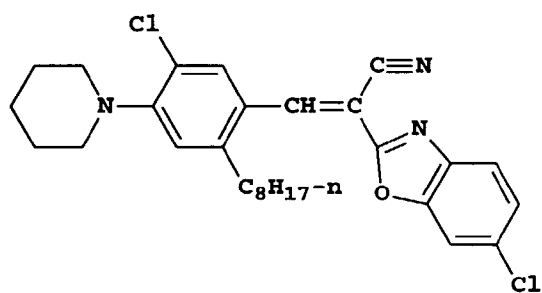
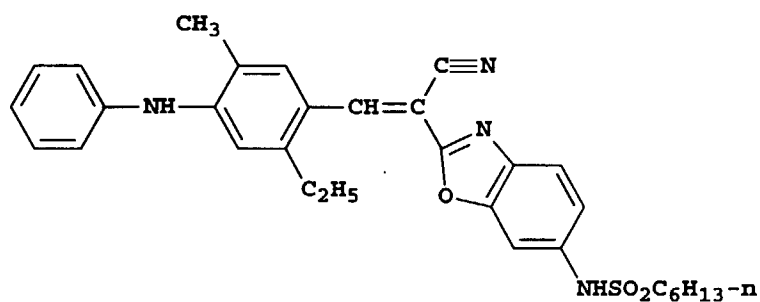


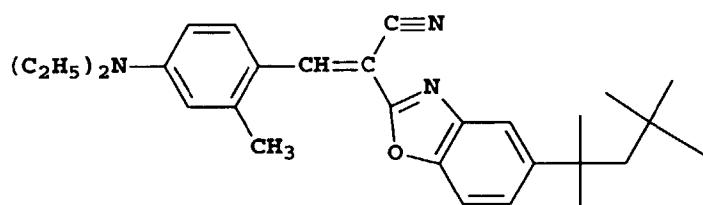
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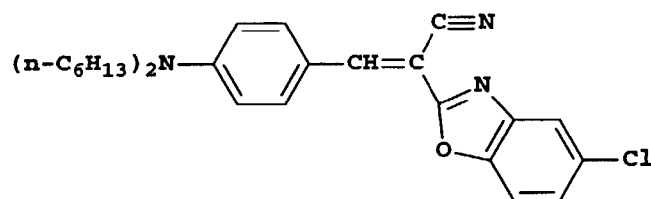
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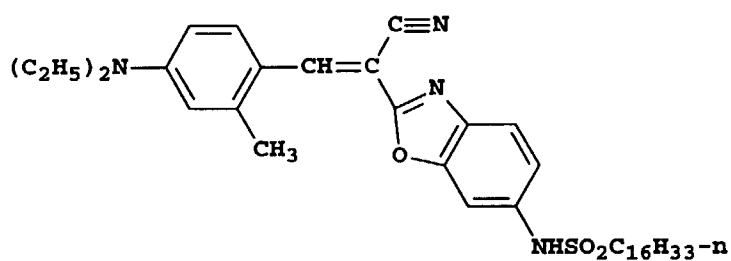




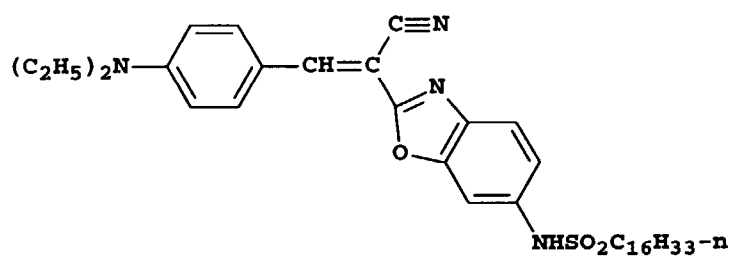
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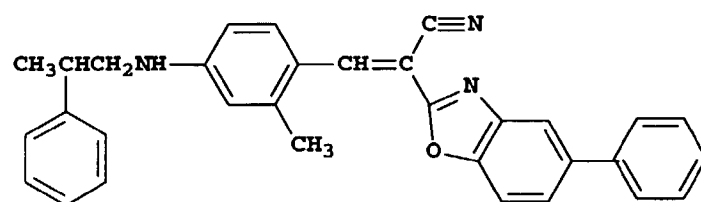
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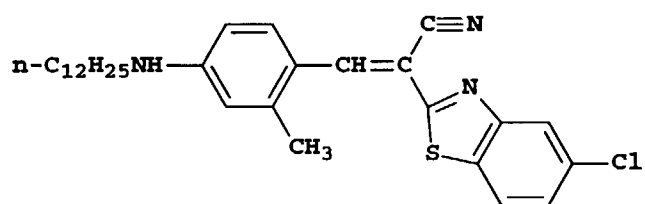
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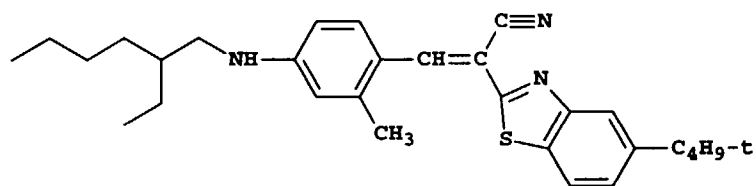
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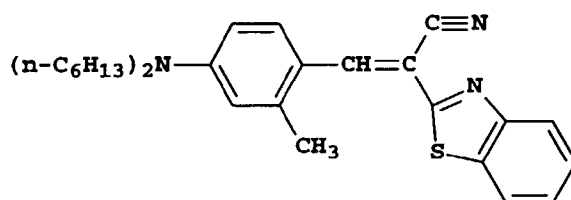
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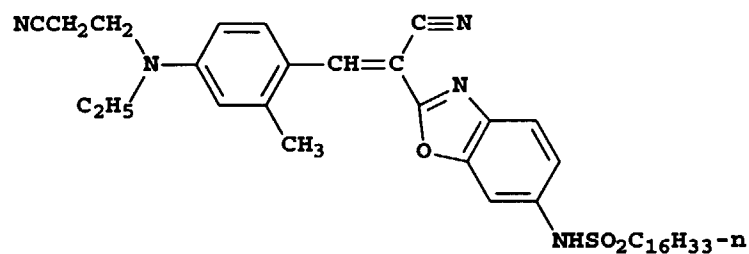
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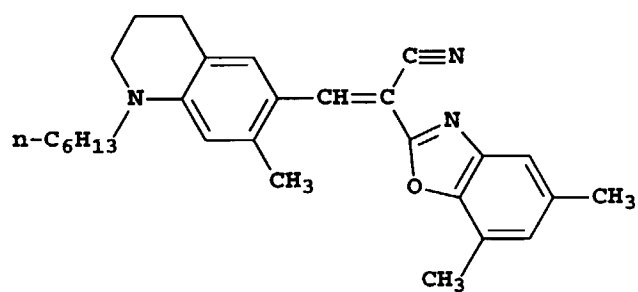
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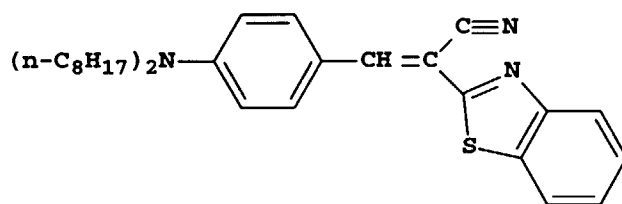
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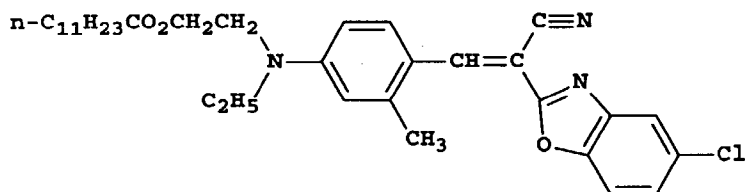
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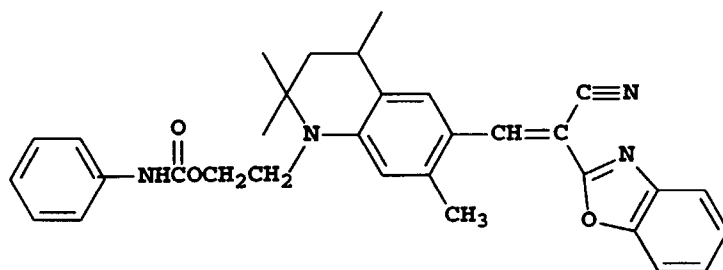
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DA33



DA34

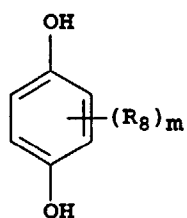


DA35

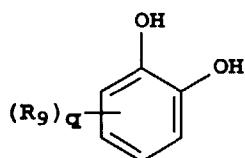
Embodiment B

This embodiment provides a multilayer color negative photographic element as in Embodiment A, at least one light-sensitive silver halide emulsion layer sensitive to each of the blue, green and red regions of the visible spectrum, one or more yellow or orange-yellow cyano benzoxazolyl or cyano benzothiazolyl arylidene type methine filter or density correction dyes of structure III, codispersed with one or more hydroquinone, catechol or sulfonamidophenol reducing agents.

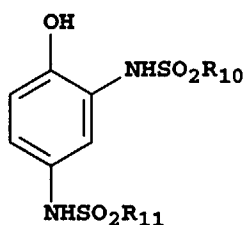
The hydroquinone, catechol and sulfonamidophenol reducing agents that are codispersed in the same oil phase with the yellow methine dyes of structure III are preferably of structures IV, V and VI, respectively,



IV



V



VI

wherein:

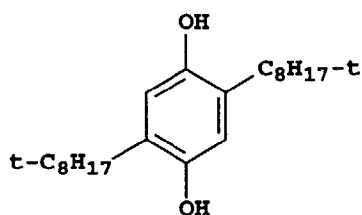
each R_8 is an independently selected from the group consisting of an alkyl group, a carbonamido group, a carbamoyl group, an alkoxy group, an aryloxy group and a chlorine atom, and m is 1 to 4;
 each R_9 is independently selected from the group consisting of an alkyl group, a carbonamido group, a carbamoyl group, an alkoxy group, an aryloxy group and a chlorine atom, and q is 1 to 4;
 R_{10} is an aryl group or an alkyl group; and
 R_{11} is an aryl group or an alkyl group.

In an embodiment of this invention the reducing agent is of structure IV, m is 2 and the R_8 groups are alkyl groups in the 2- and 5-positions of the benzene ring.

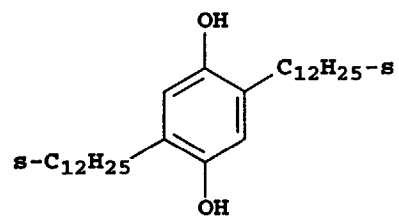
The color negative elements of this invention may be color print films used for making color prints on color photographic paper or they may be motion picture color negative films.

The alkyl substituents comprising R_8 through R_{11} may unbranched, branched or cyclic and may be unsubstituted or substituted. The alkoxy groups comprising R_8 or R_9 may be branched or unbranched and substituted or unsubstituted. The aryl groups comprising R_{10} and R_{11} and the aryloxy groups comprising R_8 and R_9 may be unsubstituted or substituted. The carbonamido and carbamoyl groups comprising R_8 and R_9 may also be unsubstituted or substituted. The carbonamido, sulfonamido, carbamoyl, acyloxy, acyl, alkoxycarbonyl, aryloxy carbonyl, sulfamoyl, sulfonyl, sulfoxyl, sulfonyloxy, alkylthio and arylthio groups comprising R_7 may also be further substituted. Any substituent may be chosen for the alkyl, aryl, alkoxy, aryloxy, R_7 , R_8 and R_9 groups that does not adversely affect the performance of the yellow methine dye formulations of this invention. Suitable substituents include halogen atoms, such as chlorine, alkenyl groups, alkynyl groups, aryl groups, hydroxy groups, alkoxy groups, aryloxy groups, acyl groups, acyloxy groups, alkoxycarbonyl groups, aryloxy carbonyl groups, carbonamido groups (including alkyl-, aryl-, alkoxy-, aryloxy- and alkylamino-carbonamido groups), carbamoyl groups, carbamoyloxy groups, sulfonamido groups, sulfamoyl groups, alkylthio groups, arylthio groups, sulfoxyl groups, sulfonyl groups, sulfonyloxy groups, alkoxysulfonyl groups, aryloxysulfonyl groups, trifluoromethyl groups, cyano groups, imido groups and heterocyclic groups, such as 2-furyl, 3-furyl, 2-thienyl, 1-pyrrolyl, 2-pyrrolyl, 1-imidazolyl and N-succinimidyl groups. The aryl groups comprising R_{10} and R_{11} and the aryloxy groups comprising R_8 and R_9 may also be substituted with one or more unbranched, branched or cyclic alkyl groups.

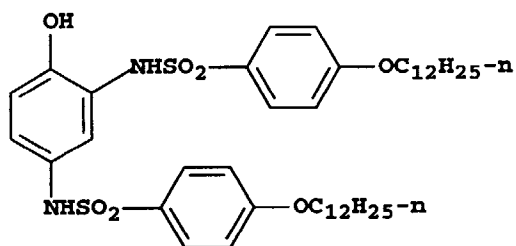
Examples of nondiffusible reducing agents (IV, V and VI) of this invention include, but are not limited to, the following (R1-R12) :



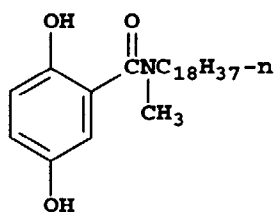
R1



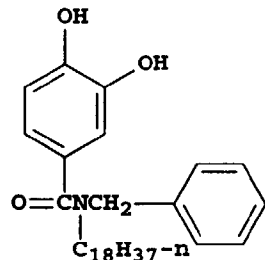
R2



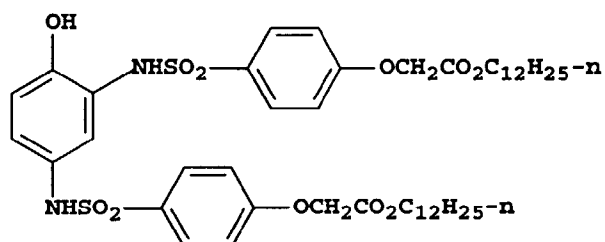
R3



R4

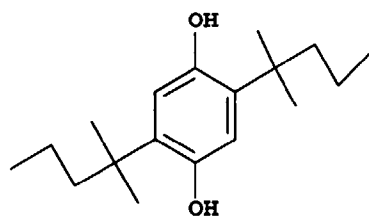


R5



R6

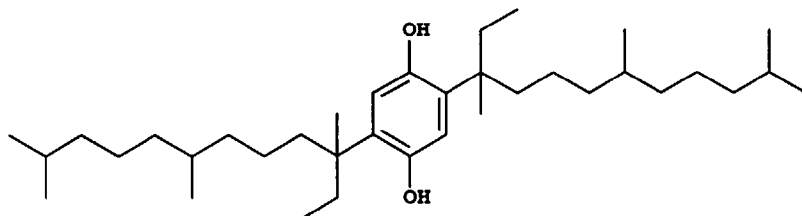
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R7

10

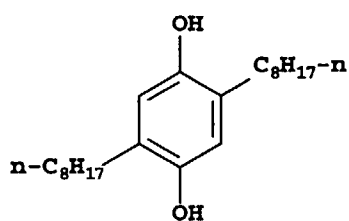
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R8

20

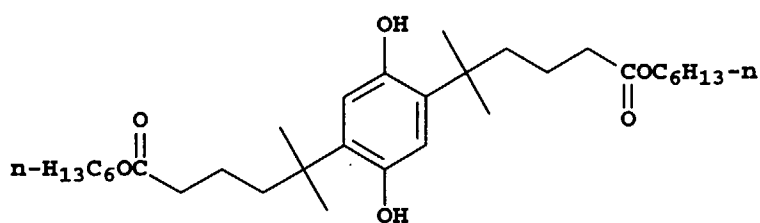
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R9

30

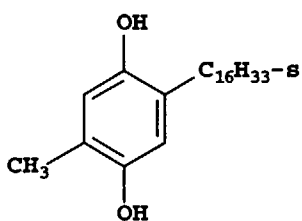
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R10

40

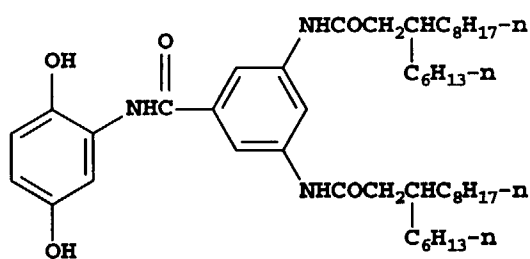
45



R11

50

55



R12

The invention has further advantages in that it provides color negatives that after long term storage continue to provide prints of the proper color balance due to use of methine dye formulations having improved thermal stability. As a further advantage, the invention provides color negative films in which some or all the conventional yellow dye (s) or Carey-Lea silver used for filtration of blue light is replaced by one or more permanent yellow filter dyes.

Additionally, it provides color negative films comprising yellow methine dyes that are used both for filtration of blue light during exposure and for density correction to provide proper color balance in printing. The provided yellow methine dyes may be used both for density correction and antihalation. Thinner color negative films are made possible by using a single yellow dye for both filtration of blue light and density correction and reduced chemical laydown can be achieved by the use of high covering power density correction dyes of the proper hue. The dye of the invention is readily dispersed. Another advantage of this invention is to provide density correction for printing of color negative films comprising magnetic recording layers.

Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituents unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the 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 or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain 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*-pentyl-phenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-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*-dodecyl-phenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-di-octadecylureido, N,N-di-octyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, 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-di-octylcarbamoyl; carbonyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxy carbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxy carbonyl, and dodecyloxy carbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxy sulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; 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-benzothiazoly; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

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.

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 PO10 7DQ, ENGLAND, and as described in Hatsumi Kyokai Koukai Gihou No. 94-6023, published March 15, 1994, available from the Japanese Patent Office, the contents of which are incorporated herein by reference. When it is desired to employ the inventive materials in a small format film, Research Disclosure, June 1994, Item 36230, provides suitable embodiments.

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 1994, Item 36544, available as described above, which will be identified hereafter 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.

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. Scan facilitating is described in Section XIV. Supports, exposure, development systems, and processing methods and agents are described in Sections XV to XX. Desirable photographic elements and processing steps including other components suitable for use in photographic elements of the invention are also described in Research Disclosure, Item 37038, February 1995.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, England, incorporated herein by reference.

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known Kodak C-41 color process as described in The British Journal of Photography Annual of 1988, pages 191-198. Where applicable, the element may be processed in accordance with color print processes such as the RA-4 process of Eastman Kodak Company as described in the British Journal of Photography Annual of 1988, Pp 198-199. Such negative working emulsions are typically sold with instructions to process using a color negative method such as the mentioned C-41 or RA-4 process. To provide a positive (or reversal) image, the color development step can be 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 E-6. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

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

Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

The entire contents of the various patent applications, patents and other publications referred to in this specification are incorporated herein by reference.

The usefulness and advantages of the yellow density correction dyes of this invention and of the color negative elements of this invention comprising the yellow density correction dyes and magnetic recording layers of this invention are illustrated by the following Examples, which show the desirable spectral properties of the yellow dyes of this invention and the improved printer compatibility of the color negative films of this invention.

Example 1

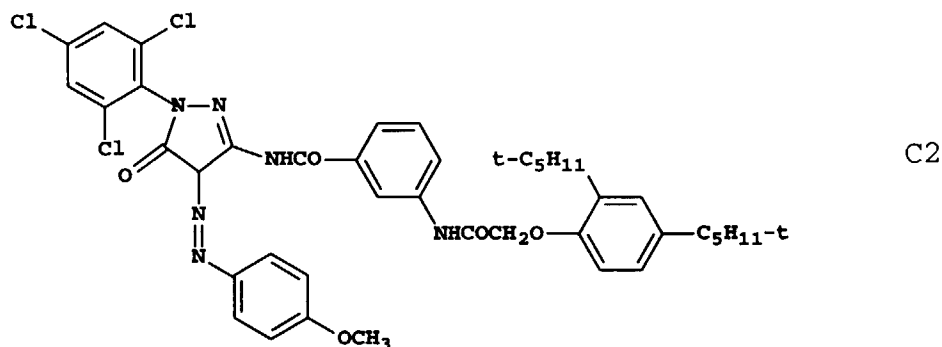
D_{min} Densities of a Conventional Color Negative Film vs a Color Negative Film Containing a Magnetic Recording Layer and Spectral Comparisons of Density Correction Dyes.

D_{min} spectra were obtained for C-41 processed color negative films coated on a conventional cellulose acetate support and on a polyethylene naphthalate support with a layer of magnetic particles. D_{min} refers to the density areas of processed film samples that received no light exposure. D_{min} densities at 420 nm, 440 nm and 480 nm are compared in Table I for a conventional 200 speed film and a similar film (referred to as Magnetic Film) on polyethylene naphthalate containing magnetic particles. The density differences between the two films are also listed in Table I. It is evident that, while the D_{min} densities for the two films are well matched at 480 nm and reasonably well matched at 440 nm, the Magnetic Film has much more density at 420 nm. This will cause some printers to increase blue light exposure through the Magnetic Film, even though color papers with a peak sensitivity near 480 nm would require the same exposure through each film to provide prints having the same color balance. The increased blue exposure of negatives on the Magnetic Film with some color printers will result in prints that are too yellow relative to prints made from conventional color negative films on most color papers.

TABLE I

| | Film | D _{min} Density | | |
|---|-----------------------------|--------------------------|-----------|-----------|
| | | at 420 nm | at 440 nm | at 480 nm |
| 1 | Magnetic Film | 1.01 | 0.99 | 0.81 |
| 2 | Conventional 200 speed film | 0.89 | 0.96 | 0.81 |
| | Difference (1 - 2) | 0.12 | 0.03 | 0.00 |

The Magnetic Film in this example contains 0.135 g/sq m of the density correction dye C2, having the structure shown below. As shown by the spectral data below, C2 has high absorption at 420 nm relative to the density correction dyes of this invention. Replacing C2 in films such as the Magnetic Film with the dyes of this invention can reduce D_{min} densities at 420 nm relative to 480 nm. This will render the density differences between films with magnetic recording layers and conventional film more similar at 420 and 480 nm. The net result is that prints made from the films with magnetic recording layers will have color balance more similar to prints made from conventional color negatives, even using printers with high sensitivity in the region of 420 nm.



To illustrate the spectral differences of conventional density correction dyes such as C2 and the yellow density correction dyes of this invention, single-layer dye coatings were prepared and evaluated. All of the density correction dyes were dispersed and coated together with the high-boiling solvent tritolyl phosphate (S-1) (mixed isomers) at a 1:2 dye to S-1 weight ratio. For example, a dispersion and coating of D1 was prepared as follows. An oil phase consisting of 8.0 g of D1, 16.0 g of S-1 and 24.0 g of ethyl acetate was added to an aqueous phase consisting of 24.0 g of gelatin 2.4 g of a surfactant (sodium triisopropylphenyl sulfonate) in 350 ml of water. The oil phase was dispersed in the aqueous phase in the form of small particles by passing the mixture through a colloid mill in a manner known in the art. The ethyl acetate auxiliary solvent was removed by evaporation resulting in a dispersion that contained 2.0% by weight of dye D1. A sample of the dispersion of D1 was coated on a transparent cellulose acetate support together with additional gelatin, a spreading agent and formaldehyde hardener at a D1 laydown of about 0.11 g/sq m to provide

a transmission optical density at the absorption maximum of about 0.7. Dispersions of the other density correction dyes were prepared similarly, and these dyes were similarly coated at levels sufficient to provide optical densities of approximately 0.7.

After hardening, the coatings were washed for 5 min at 25°C and dried. The dye absorption spectra were measured on a Perkin Elmer Lambda 2S spectrophotometer. Table II provides spectral data for the coating of comparative dye C2 with S-1 as well as for dyes D1, D2, D3 and D26 of this invention coated with S-1. Absorption maxima in nm are listed in Table II as well as density ratios at 480:420nm, 440:420 nm and 510:480 nm. It is evident from the data in Table II that the dyes of this invention have higher 480 : 420nm density ratios than dye C2. When the proper levels of dyes D1, D2, D3 or D26 of this invention are coated to achieve the desired density in the region of 480 nm where most color papers are sensitive, the resulting density in the region of 420nm will be much lower than with comparative dye C2. This will compensate for the higher absorption in the region of 420 nm due the magnetic particles (and in some cases the support) used with color negative films comprising magnetic recording layers.

TABLE II

| Dye | Absorption | D 480 nm | D 440 nm | D 510 nm |
|-----|--------------|----------|----------|----------|
| | Maximum (nm) | D 420 nm | D 420 nm | D 480 nm |
| C2 | 438 | 0.82 | 1.06 | 0.50 |
| D1 | 457 | 1.44 | 1.41 | 0.34 |
| D2 | 456 | 1.29 | 1.30 | 0.35 |
| D23 | 460 | 1.66 | 1.54 | 0.35 |
| D25 | 465 | 2.07 | 1.72 | 0.51 |
| D26 | 466 | 2.16 | 1.80 | 0.46 |

It is also desirable that density correction dyes used with color negative films comprising magnetic recording layers have somewhat higher 440 : 420nm density ratios than previously used dyes such as C2, since there is typically only a small density mismatch in the region of 440 nm between conventional color negative Dmin values and Dmin values obtained for color negative films comprising magnetic recording layers (see Table I). In addition to having 480 : 420nm density ratios that are substantially larger than the value for C2, the density correction dyes of this invention have larger 440 : 420nm density ratios, as is evident from the data in Table II. It is also desirable that yellow density correction dyes not have strong absorption at wavelengths longer than about 510 nm, particularly if they are coated above the green and red sensitive layers to filter unwanted blue light. The low 510 : 480nm density ratios for preferred density correction dyes of this invention permit their use for filtration of blue light in some instances.

An additional advantage of the density correction dyes of this invention is their relatively high covering power, which allows relatively low levels to be coated. This can reduce film cost and provide thinner films. For example, the covering power of comparative dye C2 in the coating composition of this example is only about 2.8 sq m/g, whereas the covering power values of dyes D1, D2, D3 and D26 of this invention are about 6.4, 9.6, 8.3 and 6.3 sq m/g, respectively, as coated in this example. This means that less than half as much D1, D2, D3 or D26 need be coated to achieve the same density as C2.

Example 2

Printing Characteristics of a Color Negative Film of the Invention Comprising a Magnetic Recording Layer and Yellow Density Correction Dye D1

The multilayer film structure utilized for this example is shown schematically in Table III. Structures of components not provided previously are given immediately following Table III. Component laydowns are provided in units of g/sq m unless otherwise indicated. Gelatin was used as a binder in the various layers of the multilayer film. Film A contains comparative density correction dye C2 coated at 0.086 g/sq m in the antihalation layer. Film B contains density correction dye D1 of this invention coated at 0.034 g/sq m in the antihalation layer. These films as well as the commercially available 200 speed color negative Film were given neutral exposures and processed using KODAK FLEXICOLOR C-41 processing chemistry.

The applied magnetic recording layer comprised a transparent polymeric binder, ferro-magnetic particles and abrasive particles, the magnetic particles having a surface area greater than 30 m²/gm and a coverage of from about 1x10⁻¹¹ mg/μm² to about 1x10⁻¹¹ mg/μm². The abrasive particles had a median diameter of from about 0.2 to about 0.4 μm, specific surface area greater than 5 m²/gm, a Mohs hardness of at least 6 and were present in the transparent magnetic layer in an amount of 30% and upwards by weight based on the weight of the magnetic particles present.

The neutral steps of various density were then printed onto a color paper using an AGFA MSP automatic printer that was adjusted to provide optimum color balance for prints made from the 200 speed negatives. The red, green and blue Status A densities of the prints were measured and the densities of the prints made from films A and B of Table III were compared to those of the check prints made from the 200 speed negatives. The Status A density differences are given in Tables IV and V for negatives that were normally exposed and overexposed by three stops, respectively. The density deviations are much lower for prints made from film B of this invention, which results in prints that are much less yellow than prints made from comparative film A and very similar in color balance to the prints made from the 200 speed check negatives.

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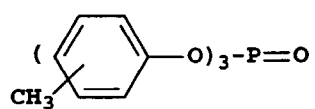
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Table III MULTILAYER FILM STRUCTURE

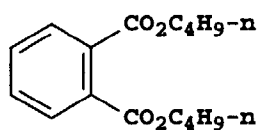
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|------------------------|---|
| 1 Overcoat Layer: | Matte Beads Gelatin (0.89) |
| 2 UV Protective Layer: | UV Absorber UV-I (0.111) & S-4 (0.111) UV Absorber UV-2 (0.111) & S-4 (0.111) Silver Bromide Lippmann Emulsion (0.215 Ag) Gelatin (0.70) |
| 3 Fast Yellow Layer: | Y-1 (0.150) & S-1 (0.075) IR-1 (0.032) & S-1 (0.016) B-1 (0.0054) & S-3 (0.0070) Blue Sensitive Silver Iodobromide Emulsion (0.430 Ag), 4.5 mole % Iodide Tabular-Grain (2.3x0.13 μ m) Gelatin (0.753) |
| 4 Slow Yellow Layer: | Y-1 (0.915) & S-1 (0.457) IR-1 (0.032) & S-1 (0.032) B-1 (0.0065) & S-3 (0.0084) Blue Sensitive Silver Iodobromide Emulsion (0.167 Ag), 4.5 mole % Iodide Tabular-Grain (1.4x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.091 Ag), 1.5 mole % Iodide Tabular-Grain (0.85x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.215 Ag), 1.3 mole % Iodide Tabular-Grain (0.54x0.09 μ m) Gelatin (1.668) Bis(vinylsulfonyl)methane Hardener at 1.8% by weight of total Gelatin |
| 5 Yellow Filter Layer: | R-1 (0.075) & S-2 (0.121) & ST-2 (0.010) YD-2 Filter Dye (0.161) Gelatin |
| 6 Fast Magenta Layer: | M-1(0.042) & S-1 (0.038) & ST-1 (0.004) Addendum MM-1 (0.027) & S-1 (0.054) IR-2 (0.016) & S-2 (0.032) Green Sensitive Silver Iodobromide Emulsion (0.699 Ag), 4.1 mole % Iodide Tabular-Grain (0.98x0.11 μ m) Gelatin (1.20) |
| 7 Mid Magenta Layer: | M-1 (0.108) & S-1 (0.097) & ST-1 (0.011) MM-1 (0.032) & S-1 (0.064) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.646 Ag), 4.1 mole % Iodide TabularGrain (0.56x0.12 μ m) Gelatin (1.52) |

| | | |
|----|--|--|
| 5 | 8 Slow Magenta Layer: | M-1 (0.323) & S-1 (0.291) & ST-1 (0.032) MM-1 (0.075) & S-1 (0.150) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.108 Ag), 3.6 mole % Iodide Cubic (0.21 μm) Green Sensitive Silver Iodobromide Emulsion (0.538 Ag), 3.7 mole % Iodide Cubic (0.11 μm) Gelatin (1.18) |
| 10 | 9 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 15 | 10 Fast Cyan Layer: | CC-1 (0.065) & S-2 (0.065) CM-1 (0.032) IR-3 (0.038) DIAR & S-5 (0.076) IR-4 (0.038) DIAR & S-2 (0.076) Red Sensitive Silver Iodobromide Emulsion (0.968 Ag), 4.5 mole % Iodide Tabular Grain (1.10x0.11 μm) Gelatin (1.45) |
| 20 | 11 Mid Cyan Layer: | CC-1 (0.183) & S-2 (0.183) CM-1 (0.011) B-1 (0.027) & S-3 (0.035) IR-3 (0.054) & S-5 (0.054) Red Sensitive Silver Iodobromide Emulsion (0.215 Ag), 4.1 mole % Iodide Tabular-Grain (1.06x0.11 μm) Red Sensitive Silver Iodobromide Emulsion (0.861 Ag), 3.3 mole % Iodide Cubic (0.49 μm) Gelatin (1.35) |
| 25 | 12 Slow Cyan Layer: | CC-1 (0.516) & S-2 (0.516) IR-3 (0.073) & S-2 (0.086) B-1 (0.075) & S-3 (0.098) Red Sensitive Silver Iodobromide Emulsion (0.473 Ag), 3.3 mole % Iodide Cubic (0.49 μm) Gelatin (1.86) |
| 30 | 13 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 35 | 14 Antihalation Layer: | Grey Silver (0.15 Ag), CD-1 (0.0075), MD-1 (0.038) R-1, S-6 (0.086) & S-6 (0.129) S-1, S-2, Gelatin (1.61) |
| 40 | | (Comparative) A C2 (0.086), (Invention) B D1 (0.034) & S-1 (0.034) |
| 45 | Polyethylene Naphthalate Support with Magnetic Recording Layer | |
| 50 | | |
| 55 | | |

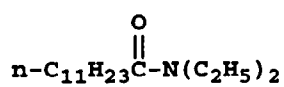


S-1

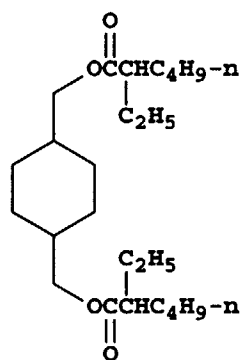
mixed isomers



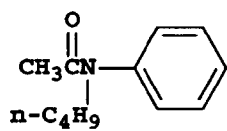
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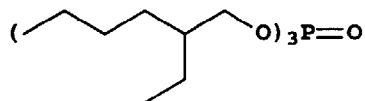
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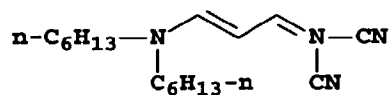
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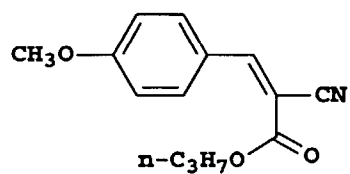
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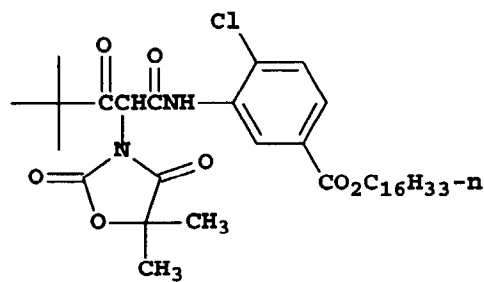
S-6



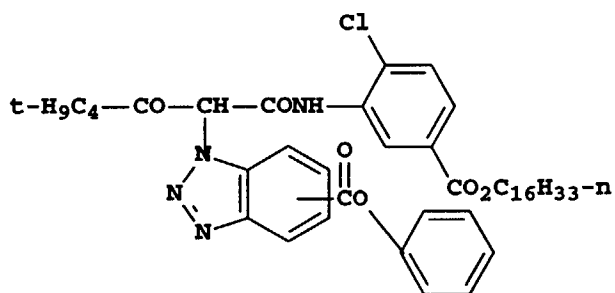
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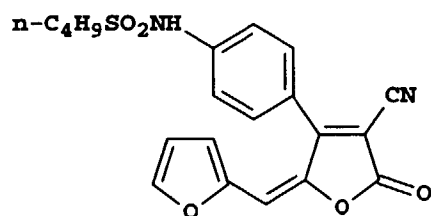
UV-2



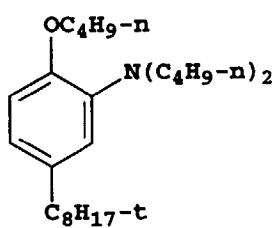
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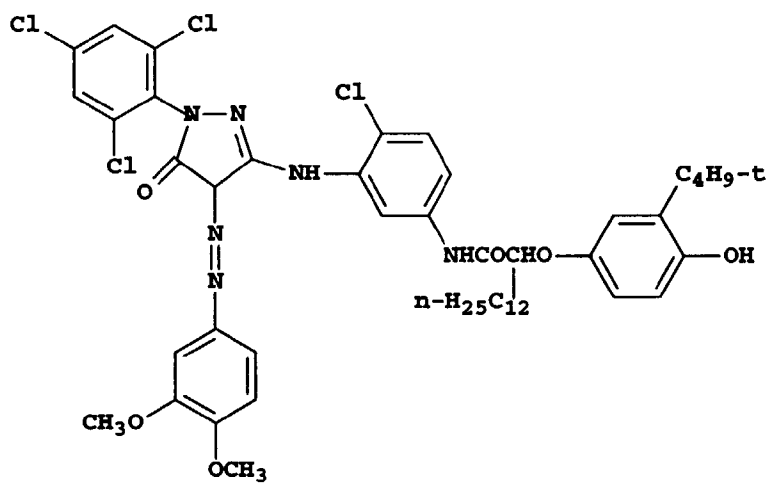
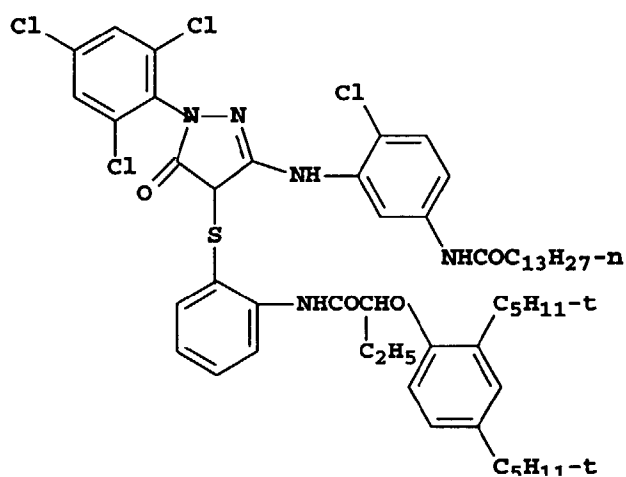
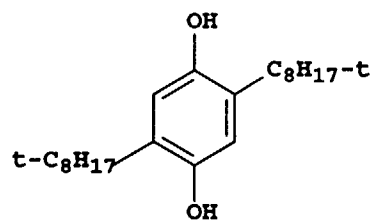
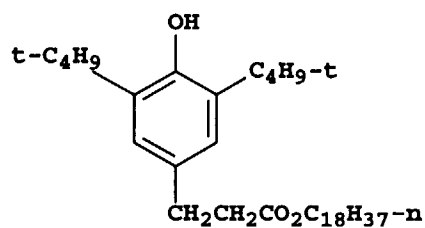
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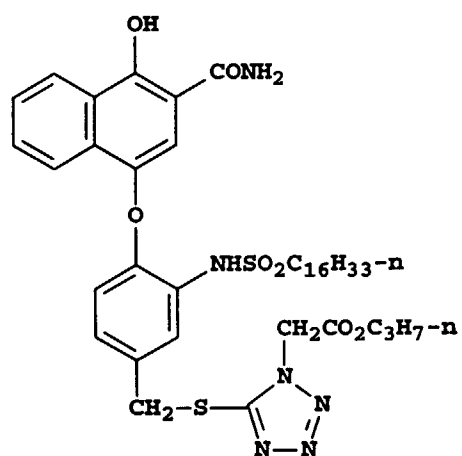
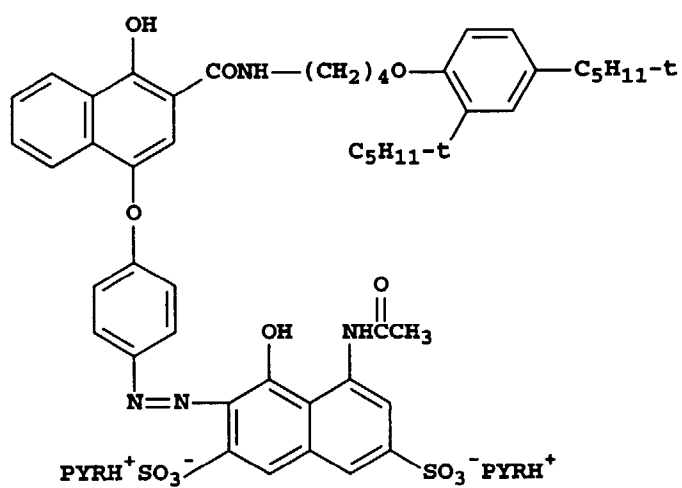
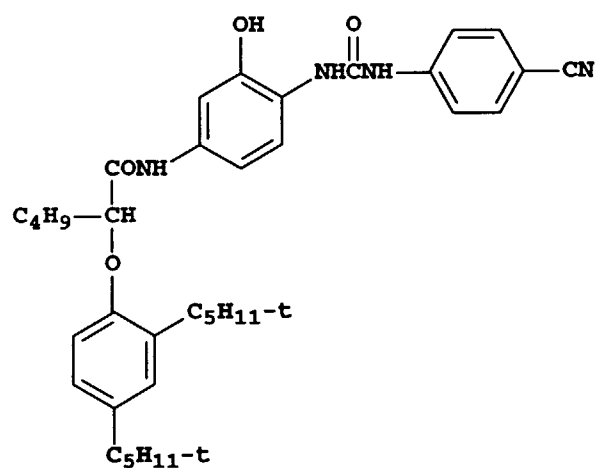


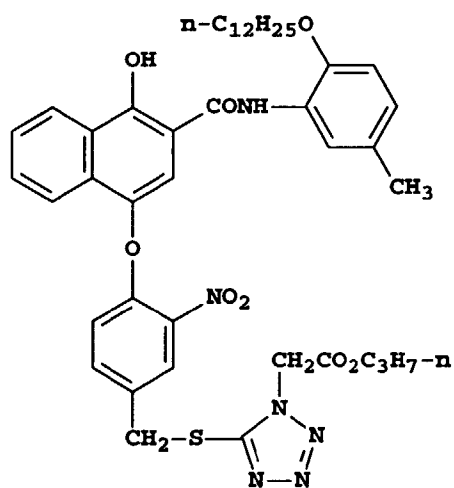
YD-2



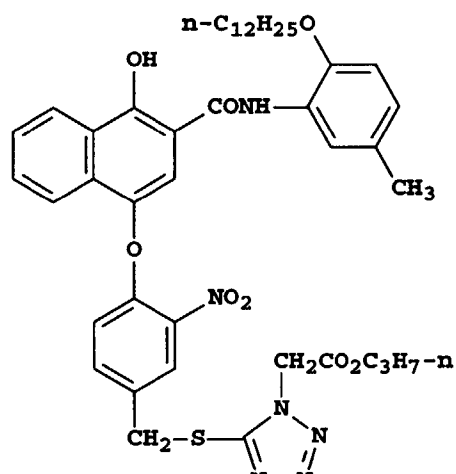
ST-1



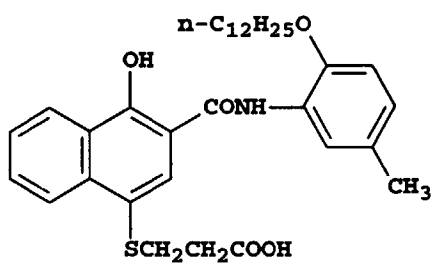




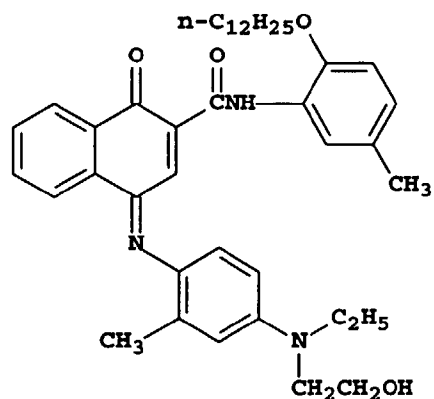
IR-3



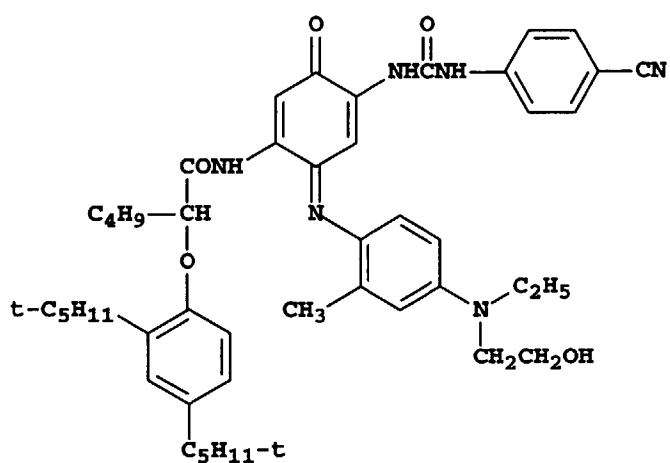
IR-4



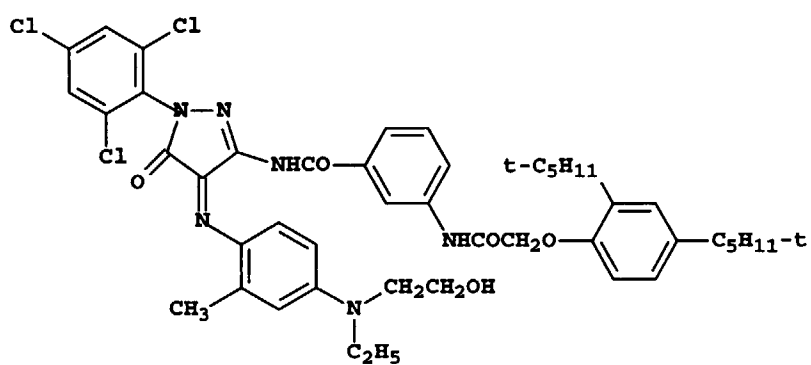
B-1



CD-1



CD-2



MD-1

TABLE IV

| | Status A Density Differences vs Prints from a Conventional 200 Speed Negative Film at Normal Exposure | | |
|-----------------|---|-------|------|
| | Red | Green | Blue |
| Multilayer Film | | | |
| A (Comparative) | -0.02 | 0.00 | 0.07 |
| B (Invention) | -0.02 | 0.01 | 0.02 |

TABLE V

| | Status A Density Differences vs Prints from 200 speed at 3 Stops Overexposure | | |
|-----------------|---|-------|------|
| Multilayer Film | Red | Green | Blue |
| A (Comparative) | -0.01 | 0.00 | 0.09 |
| B (Invention) | -0.01 | 0.00 | 0.03 |

Example 3 - Embodiment A

D_{\min} Densities of a Conventional Color Negative Film vs a Color Negative Film Containing a Magnetic Recording Layer and Spectral Comparisons of Density Correction Dyes.

D_{\min} spectra were obtained for C-41 processed color negative films coated on a conventional cellulose acetate support and on a polyethylene naphthalate support with a layer of magnetic particles. D_{\min} refers to the density areas of processed film samples that received no light exposure. D_{\min} densities at 420 nm, 440 nm and 480 nm are compared in Table VI for a conventional 200 speed film and a similar film (referred to as Magnetic Film) on polyethylene naphthalate containing magnetic particles. The density differences between the two films are also listed in Table VI. It is evident that, while the D_{\min} densities for the two films are well matched at 480 nm and reasonably well matched at 440 nm, the Magnetic Film has much more density at 420 nm. This will cause some printers to increase blue light exposure through the Magnetic Film, even though color papers with a peak sensitivity near 480 nm would require the same exposure through each film to provide prints having the same color balance. The increased blue exposure of negatives on the Magnetic Film with some color printers will result in prints that are too yellow relative to prints made from conventional color negative films on most color papers.

TABLE VI

| | | D_{\min} Density | | |
|---|-----------------------------|--------------------|-----------|-----------|
| | Film | at 420 nm | at 440 nm | at 480 nm |
| 1 | Magnetic Film | 1.01 | 0.99 | 0.81 |
| 2 | Conventional 200 speed film | 0.89 | 0.96 | 0.81 |
| | Difference (1 - 2) | 0.12 | 0.03 | 0.00 |

The Magnetic Film in this example contains 0.135 g/sq m of the density correction dye C2 as in Example I.

After hardening, the coatings were washed for 5 min at 25C and dried. The dye absorption spectra were measured on a Perkin Elmer Lambda 2S spectrophotometer. Table VII provides spectral data for the coating of comparative dye C2 with S-1 as well as for dyes DA1, DA2, DA23, DA25 and DA26 of this invention coated with S-1. Absorption maxima in nm are listed in Table VII as well as density ratios at 480:420 nm, 440:420 nm and 510:480 nm. It is evident from the data in Table VII that the dyes of this invention have higher 480:420 nm density ratios than dye C2. When the proper levels of dyes DA1, DA2, DA23, DA25 and DA26 of this invention are coated to achieve the desired density in the region of 480 nm where most color papers are sensitive, the resulting density in the region of 420 nm will be much lower than with comparative dye C2. This will compensate for the higher absorption in the region of 420 nm due the magnetic particles (and in some cases the support) used with color negative films comprising magnetic recording layers.

TABLE VII

| Dye | Absorption | D 480 nm | D 440 nm | D 510 nm |
|------|--------------|----------|----------|----------|
| | Maximum (nm) | D 420 nm | D 420 nm | D 480 nm |
| C2 | 438 | 0.82 | 1.06 | 0.50 |
| DA1 | 457 | 1.44 | 1.41 | 0.34 |
| DA2 | 456 | 1.29 | 1.30 | 0.35 |
| DA23 | 460 | 1.66 | 1.54 | 0.35 |
| DA25 | 465 | 2.07 | 1.72 | 0.51 |
| DA26 | 466 | 2.16 | 1.80 | 0.46 |

Another advantage of the yellow methine density correction dyes of this invention is their excellent stability on

storage. For example, dye D1 (coated with S-1 at 1:2) undergoes less than 2% density loss after storage for one week at 70°C/50% RH, whereas dye C1 noted earlier loses 50% of its original density (coated with S-1 at 1:2) after storage for one week at 70°C/50% RH. The yellow methine density correction dyes of this invention also show improved stability over dye C2 and analogs when coated in the same layer as reducing agents such as 2,5-di-*t*-octyl hydroquinone.

Example 4

Printing Characteristics of a Color Negative Film of this Invention Comprising a Magnetic Recording Layer and Yellow Methine Density Correction Dye DA1 of this Invention

The multilayer film structure utilized for this example is shown schematically in Table VIII. Film A contains comparative density correction dye C2 at 0.140 g/sq m, of which 0.097 g/sq m is coated in the yellow filter layer between the blue and green sensitive layers and 0.043 g/sq m is coated in the antihalation layer just above the support. Film B contains 0.097 g/sq m of C1 in the yellow filter layer plus 0.011 g/sq m of C2 and 0.027 g/sq m of C1 in the antihalation layer. Film C of this invention contains 0.039 g/sq m of density correction dye DA1 of this invention in the yellow filter layer and no yellow density correction dye in the antihalation layer. These films as well as commercially available 200 speed Color Negative Film were given neutral exposures and processed using KODAK FLEXICOLOR C-41 processing chemistry.

The neutral steps of various density were then printed onto color paper using an AGFA MSP automatic printer that was adjusted to provide optimum color balance for prints made from the 200 speed negatives. The red, green and blue Status A densities of the prints were measured and the densities of the prints made from films A, B and C of Table III were compared to those of the check prints made from the 200 speed negatives. The Status A density differences are given in Tables IX and X for negatives that were normally exposed and overexposed by three stops, respectively. The density deviations are much lower for prints made from film C of this invention. The reduction on the blue density differences for film C are particularly significant and result in prints that are much less yellow than prints made from films B or C, and very similar in color balance to the prints made from the 200 speed check negatives.

Table VIII MULTILAYER FILM STRUCTURE

| | |
|--------------------------|-----------------------|
| 1 Overcoat Layer: | Matte Beads |
| | Gelatin (0.89) |

| | | |
|----|------------------------|--|
| 5 | 2 UV Protective Layer: | UV Absorber UV-1 (0.111) & S-4 (0.111) UV Absorber UV-2 (0.111) & S-4 (0.111) Silver Bromide Lippmann Emulsion (0.215 Ag) Gelatin (0.70) |
| 10 | 3 Fast Yellow Layer: | Y-1 (0.150) & S-1 (0.075) IR-1 (0.032) & S-1 (0.016) B-1 (0.0054) & S-3 (0.0070) Blue Sensitive Silver Iodobromide Emulsion (0.430 Ag), 4.5 mole % Iodide Tabular-Grain (2.3x0.13 µm) Gelatin (0.753) |
| 15 | 4 Slow Yellow Layer: | Y-1 (0.915) & S-1 (0.457) IR-1 (0.032) & S-1 (0.032) B-1 (0.0065) & S-3 (0.0084) Blue Sensitive Silver Iodobromide Emulsion (0.161 Ag), 4.5 mole % Iodide Tabular-Grain (1.4x0.13 µm) Blue Sensitive Silver Iodobromide Emulsion (0.108 Ag), 1.5 mole % Iodide Tabular-Grain (0.85x0.13 µm) Blue Sensitive Silver Iodobromide Emulsion (0.161 Ag), 1.3 mole % Iodide Tabular-Grain (0.54x0.09 µm) Gelatin (1.668) Bis(vinylsulfonyl)methane Hardener at 1.8% by weight of total Gelatin |
| 20 | 5 Yellow Filter Layer: | R-1 (0.075) & S-2 (0.121) & ST-2 (0.010) YD-2 (0.108) Gelatin (0.861) & A C2 (0.097) or B C2 (0.097) or C DA1 (0.039) & S-1 (0.078) |
| 25 | 6 Fast Magenta Layer: | M-1(0.052) & S-1 (0.047) & ST-1 (0.005) MM-1 (0.027) & S-1 (0.054) IR-2 (0.016) & S-2 (0.032) Green Sensitive Silver Iodobromide Emulsion (0.699 Ag), 4.5 mole % Iodide Tabular-Grain (0.98x0.11 µm) Gelatin (1.12) |
| 30 | 7 Mid Magenta Layer: | M-1 (0.099) & S-1 (0.089) & ST-1 (0.010) MM-1 (0.032) & S-1 (0.064) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.646 Ag), 4.5 mole % Iodide TabularGrain (0.61x0.12 µm) Gelatin (1.41) |
| 35 | 8 Slow Magenta Layer: | M-1 (0.204) & S-1 (0.184) & ST-1 (0.020) MM-1 (0.038) & S-1 (0.076) Green Sensitive Silver Iodobromide Emulsion (0.258 Ag), 1.5 mole % Iodide TabularGrain (0.70x0.11 µm) Green Sensitive Silver Iodobromide Emulsion (0.409 Ag), 1.3 mole % Iodide TabularGrain (0.54x0.09 µm) Gelatin (1.18) |
| 40 | | |
| 45 | | |
| 50 | | |
| 55 | | |

| | |
|---|--|
| 9 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 10 Fast Cyan Layer: | CC-1 (0.161) & S-2 (0.161) CM-1 (0.032) IR-3 (0.038) DIAR & S-5 (0.038) IR-4 (0.038) DIAR & S-2 (0.076) Red Sensitive Silver Iodobromide Emulsion (1.08 Ag), 4.5 mole % Iodide TabularGrain (1.10x0.11 μ m) Gelatin (1.45) |
| 11 Mid Cyan Layer: | CC-1 (0.183) & S-2 (0.183) CM-1 (0.011) B-1 (0.027) & S-3 (0.035) IR-3 (0.054) & S-5 (0.054) Red Sensitive Silver Iodobromide Emulsion (0.215 Ag), 4.5 mole % Iodide Tabular-Grain (0.98x0.11 μ m) Red Sensitive Silver Iodobromide Emulsion (0.861 Ag), 3.3 mole % Iodide Cubic (0.49 μ m) Gelatin (1.35) |
| 12 Slow Cyan Layer: | CC-1 (0.355) & S-2 (0.355) IR-4 (0.011) & S-2 (0.022) B-1 (0.075) & S-3 (0.098) Red Sensitive Silver Iodobromide Emulsion (0.387 Ag), 3.3 mole % Iodide Cubic (0.32 μ m) Gelatin (1.64) |
| 13 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 14 Antihalation Layer: | Grey Silver (0.15 Ag), CD-1 (0.0075), MD-1 (0.032) S-1, S-6 (0.323), Gelatin (1.61) & A C2 (0.043), or B C2 (0.011) & C1 (0.027) & S-1 (0.054), or C No additional yellow density correction dye in AHU |
| <u>Polyethylene Naphthalate Support with Magnetic Recording Layer</u> | |

TABLE IX

| Status A Density Differences vs Prints from Commercial 200 Speed Film at Normal Exposure | | | |
|--|-------|-------|------|
| Multilayer Film | Red | Green | Blue |
| A (Comparative) | -0.04 | 0.00 | 0.07 |
| B (Comparative) | -0.03 | 0.00 | 0.03 |
| C (Invention) | -0.02 | 0.01 | 0.00 |

TABLE X

| | Status A Density Differences vs Prints from 200 speed at 3 Stops Overexposure | | |
|-----------------|---|-------|------|
| Multilayer Film | Red | Green | Blue |
| A (Comparative) | -0.01 | 0.00 | 0.09 |
| B (Comparative) | -0.02 | 0.00 | 0.06 |
| C (Invention) | -0.00 | 0.00 | 0.03 |

Example 5

Printing Characteristics of Color Negative Films of this Invention Comprising a Magnetic Recording Layer and Yellow Methine Density Correction Dyes DA1 and DA23 of this Invention in the AHU.

Another set of multilayer films was prepared that included a comparative film and films containing density correction dyes DA1 or DA23 of this invention. The multilayer films were coated on the same support and with the same magnetic recording layer as the films of Example 4. The coating structure of these films is similar to that of Example 4, except that the yellow filter layer (5) is as shown in Table XI, below, and the antihalation layer (14) varies as also shown in Table XI. Comparative film D contains 0.151 g/sq m of density correction dye C2 in the antihalation layer, whereas film E of this invention contains 0.038 g/sq m of dye DA1 in the antihalation layer and film F of this invention contains 0.037 g/sq m of density correction dye DA23 in the antihalation layer. These films as well as the commercially available 200 speed color negative Film were given neutral exposures and processed using KODAK FLEXICOLOR C-41 processing chemistry.

The neutral steps of various density were then printed onto color paper using an AGFA MSP automatic printer that was adjusted to provide optimum color balance for prints made from the 200 speed negatives. The red, green and blue Status A densities of the prints were measured and the densities of the prints made from films D, E and F of Table VI were compared to those of the check prints made from the 200 speed negatives. The Status A density differences are given in Table XII for negatives given a normal neutral exposure. It is evident that the density deviations are much lower for prints made from film E and F of this invention. The reductions in the blue density differences for prints from films E and F are particularly significant and result in prints that are much less yellow than those made from film D and very similar in color balance to prints made from the 200 speed check negatives.

TABLE XI

| | |
|------------------------|--|
| 5 Yellow Filter Layer: | R-1 (0.075) & S-2 (0.121) & ST-2 (0.010) YD-2 (0.161) Gelatin (0.861) |
| 14 Antihalation Layer: | Grey Silver (0.15 Ag), CD-1 (0.0075), MD-1 (0.032) S-1, S-6 (0.323), Gelatin (1.61) & D C2(0.151) or E DA1 (0.038) & (0.076) S-1 or F DA23 (0.037) & (0.148) S-1 |

TABLE XII

| | Status A Density Differences vs Prints from 200 speed color negative film at Normal Exposure | | |
|-----------------|--|-------|-------|
| Multilayer Film | Red | Green | Blue |
| D (Comparative) | -0.02 | 0.00 | 0.07 |
| E (Invention) | 0.00 | -0.01 | 0.01 |
| F (Invention) | 0.00 | 0.00 | -0.01 |

Example 6

Printing Characteristics of Color Negative Films of this Invention Comprising a Magnetic Recording Layer and Yellow Methine Density Correction Dye DA23 of this Invention

Another set of multilayer films was prepared that included a comparative film and films containing density correction dye DA23 of this invention. The multilayer films were coated on the same support and with the same magnetic recording layer as the films of Example 4 with a similar coating structure, as shown in Table XIII. Comparative film G contains 0.097 g/sq m of C2 in the yellow filter layer and 0.043 g/sq m of C2 in the antihalation layer (14). Film H of this invention contains dye DA23 in the antihalation layer at 0.0365 g/sq m and film I of this invention contains 0.0365 g/sq m of dye DA23 in the slow magenta layer (8). These films as well as commercially available 200 speed color negative film were given neutral exposures and processed using KODAK FLEXICOLOR C-41 processing chemistry.

The neutral steps of various density were then printed onto color print paper using an AGFA MSP automatic printer that was adjusted to provide optimum color balance for prints made from the 200 speed negatives. The red, green and blue Status A densities of the prints were measured and the densities of the prints made from films G, H and I of Table XIII were compared to those of the check prints made from the 200 speed negatives. The Status A density differences are given in Table XIV for negatives given a normal neutral exposure. It is evident that the density deviations are much lower for prints made from films H and I of this invention. The reduction in the blue density differences for prints from films H and I are particularly significant and result in prints that, rather than being yellow like those from film G, are very similar in color balance to the prints made from the 200 speed check negatives.

Table XIII MULTILAYER FILM STRUCTURE

| | |
|------------------------|---|
| 1 Overcoat Layer: | Matte Beads Gelatin (0.89) |
| 2 UV Protective Layer: | UV Absorber UV-1 (0.111) & S-4 (0.111) UV Absorber UV-2 (0.111) & S-4 (0.111) Silver Bromide Lippmann Emulsion (0.215 Ag) Gelatin (0.70) |
| 3 Fast Yellow Layer: | Y-1 (0.150) & S-1 (0.075) IR-1 (0.032) & S-1 (0.016) B-1 (0.0054) & S-3 (0.0070) Blue Sensitive Silver Iodobromide Emulsion (0.430 Ag), 4.5 mole % Iodide Tabular-Grain (2.3x0.13 μ m) Gelatin (0.753) |
| 4 Slow Yellow Layer: | Y-1 (0.915) & S-1 (0.457) IR-1 (0.032) & S-1 (0.016) B-1 (0.0065) & S-3 (0.0084) Blue Sensitive Silver Iodobromide Emulsion (0.178 Ag), 4.5 mole % Iodide Tabular-Grain (1.4x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.118 Ag), 1.5 mole % Iodide Tabular-Grain (0.85x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.178 Ag), 1.3 mole % Iodide Tabular-Grain (0.54x0.09 μ m) Gelatin (1.668) Bis(vinylsulfonyl)methane Hardener at 1.8% by weight of total Gelatin |

| | | |
|----|------------------------|---|
| 5 | 5 Yellow Filter Layer: | R-1 (0.075) & S-2 (0.121) & ST-2 (0.010) Gelatin (0.861) & G C2 (0.097) & YD-2 Filter Dye (0.108) or H No yellow density correction dye & YD-2 (0.161) or I No yellow density correction dye & YD-2 (0.161) |
| 10 | 6 Fast Magenta Layer: | M-1(0.059)& S-1 (0.053) & ST-1 (0.006) Addendum MM-1 (0.027) & S-1 (0.054) IR-2 (0.016) & S-2 (0.032) Green Sensitive Silver Iodobromide Emulsion (0.699 Ag), 4.5 mole % Iodide Tabular-Grain (0.98x0.11 µm) Gelatin (1.22) |
| 20 | 7 Mid Magenta Layer: | M-1 (0.124) & S-1 (0.111) & ST-1 (0.012) MM-1 (0.032) & S-1 (0.064) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.646 Ag), 4.5 mole % Iodide TabularGrain (0.61x0.12 µm) Gelatin (1.41) |
| 25 | 8 Slow Magenta Layer: | M-1 (0.172) & S-1 (0.155) & ST-1 (0.017) MM-1 (0.038) & S-1 (0.076) Green Sensitive Silver Iodobromide Emulsion (0.377 Ag), 3.3 mole % Iodide Cubic (0.275 µm) Green Sensitive Silver Iodobromide Emulsion (0.108 Ag), 1.3 mole % Iodide TabularGrain (0.54x0.09 µm) Gelatin (1.18) & G No yellow density correction dye or H No yellow density correction dye or I D23 (0.0365) + S1 (0.146) |
| 30 | 9 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 35 | 10 Fast Cyan Layer: | CC-1 (0.172) & S-2 (0.172) CM-1 (0.032) IR-3 (0.038) & S-5 (0.076) IR-4 (0.038) & S-2 (0.076) Red Sensitive Silver Iodobromide Emulsion (0.968 Ag), 4.5 mole % Iodide Tabular-Grain (1.10x0.11 µm) Gelatin (1.45) |

| | |
|--|--|
| 11 Mid Cyan Layer: | CC-1 (0.183) & S-2 (0.183) CM-1 (0.011) B-1 (0.027) & S-3 (0.035) IR-3 (0.054) & S-5 (0.108) Red Sensitive Silver Iodobromide Emulsion (0.215 Ag), 4.5 mole % Iodide Tabular-Grain (0.98x0.11 μ m) Red Sensitive Silver Iodobromide Emulsion (0.861 Ag), 3.3 mole % Iodide Cubic (0.49 μ m) Gelatin (1.35) |
| 12 Slow Cyan Layer: | CC-1 (0.355) & S-2 (0.355) IR-4 (0.011) & S-2 (0.022) B-1 (0.075) & S-3 (0.098) Red Sensitive Silver Iodobromide Emulsion (0.387 Ag), 3.3 mole % Iodide Cubic (0.32 μ m) Gelatin (1.64) |
| 13 Interlayer: | R-1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 14 Antihalation Layer: | Grey Silver (0.15 Ag), CD-2 (0.0075), MD-1 (0.038) R-1 (0.108), S-1, S-2, S-6 (.161), Gelatin (1.61) & G C2 (0.043) or H DA23 (0.0365) and S-1(0.146) or I No additional yellow density correction dye in AHU |
| Polyethylene Naphthalate Support with Magnetic Recording Layer | |

TABLE XIV

| | Status A Density Differences vs Prints from conventional 200 speed negative film at Normal Exposure | | |
|-----------------|---|-------|------|
| Multilayer Film | Red | Green | Blue |
| G (Comparative) | -0.02 | 0.00 | 0.09 |
| H (Invention) | 0.00 | 0.01 | 0.00 |
| I (Invention) | 0.00 | 0.00 | 0.00 |

Example 7

Preparation and Properties of Codispersions of Yellow Dye DA23 and Reducing Agent R₁ of This Invention.

To prepare dispersions of yellow dye DA23, 4.0 g of DA23 was dissolved in 8.0g of tricresylphosphate (S-1) and 12.0 g of ethyl acetate at 75°C. This oil phase was then combined with an aqueous phase solution consisting of 8.0 g of gelatin, 6.0 g of a 10% solution of Alkanol-XC (Dupont), and 62.0 g of distilled water. This mixture was then passed through a Gaulin colloid mill five times followed by removal of ethyl acetate by rotary evaporation. Distilled water was then added back to replace the ethyl acetate to form Dispersion A which consisted of 4.0% dye and 8.0% gelatin. Dispersion B was prepared similarly except that 2.0 of 2,5-di-octylhydroquinone (R1) was also dissolved in the oil phase and 60.0 g of distilled water was used in the aqueous phase. Dispersion C was similarly prepared using 4.0 g of R1 in the oil phase and 58.0 g of distilled water in the aqueous phase. Dispersion D was also similarly prepared using 8.0 g of R1 in the oil phase and 54.0 g of distilled water in the aqueous phase. These dispersions were held for

96 hours at 45°C and then examined for dye crystallization using polarized-light microscopy. Results are summarized below in Table I.

Table XV

| Dispersion | Microscopic Appearance (96h/45°C) |
|----------------|---|
| A (Comparison) | Severe crystallization, many long needles |
| B (Invention) | Some crystallization, several small needles |
| C (Invention) | Very few small needle-shaped crystals |
| D (Invention) | Some crystallization, several small plates |

These results clearly show that the presence of R1 in the oil phase substantially reduces the propensity for dye crystallization in the codispersions (B-D) of this invention. This allows such dispersions to be coated in multilayer color negative films using normal melt hold times (of about 4 hours) with little or no crystallization.

Coatings of these dispersions on cellulose triacetate were prepared in which the DA23 laydown was sufficient (about 0.12 g/sq m) to yield an optical density at the absorption maximum of about 1.1. The absorption spectra of the films were measured using a Perkin Elmer Lambda 2S spectrophotometer. Spectral results are summarized in Table XVI, below.

Table XVI

| Dispersion | Density @ 420 nm | Lambda-max |
|------------|------------------|------------|
| A | 0.69 | 462nm |
| B | 0.65 | 462nm |
| C | 0.61 | 466nm |
| D | 0.50 | 470nm |

These data clearly indicate that the presence of R1 in the oil phase with dye DA23 results in lower densities in the short blue wavelength region of the spectrum and a bathochromic hue shift. Both of these features are desirable for density correction in many color negative films, especially in films comprising magnetic recording layers.

Example 8

Additional Dye/Reducing Agent Codispersions of This Invention

Dispersions E, F, and G were prepared as Dispersions A, C, and D, respectively, except that tricresylphosphate was replaced with tri-(2-ethylhexyl)phosphate (S-6). These dispersions were held for four hours at 45°C and then examined for dye crystallization. Results are summarized below in Table III.

Table XVII

| Dispersion | Microscopic Appearance (4h/45°C) |
|----------------|--|
| E (Comparison) | Severe crystallization, many small needles |
| F (Invention) | Some small needle-shaped crystals |
| G (Invention) | Few small plate-like crystals |

These results also indicate that improved dispersion stability is obtained by codispersing R1 in the oil phase with dye DA23.

These dispersions were also coated and their spectral properties were determined as described in Example 1. The results are given below in Table XVIII.

TABLE XVIII

| Dispersion | Density @ 420nm | Lambda-max |
|------------|-----------------|------------|
| D | 0.85 | 447nm |
| E | 0.79 | 449nm |
| F | 0.68 | 456nm |

These results also indicate that the DA23 dye hue is shifted bathochromically and absorption in the short blue region is reduced as the level of R1 is increased.

Example 9

A Multilayer Color Negative Film of This Invention Comprising a Yellow Methine Dye of This Invention Codispersed with a Reducing Agent of This Invention.

The multilayer film structure utilized for this example is shown schematically in Table XIX. Structures of components not provided previously are given immediately following Table XIX. Component laydowns are provided in units of g/sq m unless otherwise indicated. Gelatin was used as a binder in the various layers of the multilayer film. These films may be processed using KODAK FLEXICOLOR C-41 processing chemistry. The film was readily manufactured and produced prints of proper color balance.

Table XIX MULTILAYER FILM STRUCTURE

| | |
|------------------------|---|
| Overcoat Layer: | Matte Beads Gelatin (0.89) |
| 2 UV Protective Layer: | UV-1 (0.111) & S-4 (0.111) UV-2 (0.111) & S-4 (0.111) Silver Bromide Lippmann Emulsion (0.215 Ag) Gelatin (0.70) |
| 3 Fast Yellow Layer: | Y-1 (0.150) & S-1 (0.075) IR-1 (0.032) & S-1 (0.016) B-1 (0.0054) & S-3 (0.0070) Blue Sensitive Silver Iodobromide Emulsion (0.430 Ag), 4.5 mole % Iodide T-Grain (2.3x0.13 μ m) Gelatin (0.753) |
| 4 Slow Yellow Layer: | Y-1 (0.915) & S-1 (0.457) IR-1 (0.032) & S-1 (0.032) B-1 (0.0065) & S-3 (0.0084) Blue Sensitive Silver Iodobromide Emulsion (0.167 Ag), 4.5 mole % Iodide T-Grain (1.4x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.091 Ag), 1.5 mole % Iodide T-Grain (0.85x0.13 μ m) Blue Sensitive Silver Iodobromide Emulsion (0.215 Ag) 1.3 mole % Iodide T-Grain (0.54x0.09 μ m) Gelatin (1.668) Bis(vinylsulfonyl)methane at 1.8% by weight of total Gelatin |
| 5 Yellow Filter Layer: | R1 (0.075) & S-2 (0.121) & ST-2 (0.010) YD-2 (0.161) Gelatin (0.861) |
| 6 Fast Magenta Layer: | M-1(0.042) & S-1 (0.038) & ST-1 (0.004) Addendum MM-1 (0.027) & S-1 (0.054) IR-2 (0.016) & S-2 (0.032) Green Sensitive Silver Iodobromide Emulsion (0.699 Ag), 4.1 mole % Iodide T-Grain (0.98x0.11 μ m) Gelatin (1.20) |

| | | |
|----|--|--|
| 5 | 7 Mid Magenta Layer: | M-1 (0.108) & S-1 (0.097) & ST-1 (0.011) MM-1 (0.032) & S-1 (0.064) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.646 Ag), 4.1 mole % Iodide T-Grain (0.56x0.12 μm) Gelatin (1.52) |
| 10 | 8 Slow Magenta Layer: | M-1 (0.323) & S-1 (0.291) & ST-1 (0.032) MM-1 (0.075) & S-1 (0.150) IR-2 (0.022) & S-2 (0.044) Green Sensitive Silver Iodobromide Emulsion (0.108 Ag), 3.6 mole % Iodide Cubic (0.21 μm) Green Sensitive Silver Iodobromide Emulsion (0.538 Ag), 3.7 mole % Iodide Cubic (0.11 μm) Gelatin (1.18) |
| 20 | 9 Interlayer: | R1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 25 | 10 Fast Cyan Layer: | CC-1 (0.065) & S-2 (0.065) CM-1 (0.032) IR-3 (0.038) & S-5 (0.076) IR-4 (0.038) & S-2 (0.076) Red Sensitive Silver Iodobromide Emulsion (0.968 Ag), 4.5 mole % Iodide T-Grain (1.10x0.11 μm) Gelatin (1.45) |
| 30 | 11 Mid Cyan Layer: | CC-1 (0.183) & S-2 (0.183) CM-1 (0.011) B-1 (0.027) & S-3 (0.035) IR-3 (0.054) & S-5 (0.108) Red Sensitive Silver Iodobromide Emulsion (0.215 Ag), 4.1 mole % Iodide T-Grain (1.06x0.11 μm) Red Sensitive Silver Iodobromide Emulsion (0.861 Ag), 3.3 mole % Iodide Cubic (0.49 μm) Gelatin (1.35) |
| 40 | 12 Slow Cyan Layer: | CC-1 (0.516) & S-2 (0.516) IR-3 (0.043) & S-2 (0.086) B-1 (0.075) & S-3 (0.098) Red Sensitive Silver Iodobromide Emulsion (0.473 Ag), 3.3 mole % Iodide Cubic (0.32 μm) Gelatin (1.86) |
| 50 | 13 Interlayer: | R1 (0.075) & S-6 (0.113) Gelatin (0.86) |
| 55 | 14 Antihalation Layer: | Grey Silver (0.15 Ag), CD-2 (0.0075), MD-1 (0.038) R1 (0.086) & S-6 (0.129) S-1, S-2, Gelatin (1.61) Codispersion of DA23 (0.022) & R1 (0.022) & S-1 (0.044) |
| | Polyethylene Naphthalate Support with Magnetic Recording Layer | |

The preceding examples are set forth to illustrate specific embodiments of this invention and are not intended to limit the scope of the compositions or materials of the invention. Additional embodiments and advantages within the scope of the claimed invention will be apparent to one skilled in the art.

Claims

1. A multilayer color negative photographic element comprising a support, at least one light-sensitive silver halide emulsion layer sensitive to each of the blue, green and red regions of the visible spectrum, a magnetic recording layer, and a permanent dye, wherein:

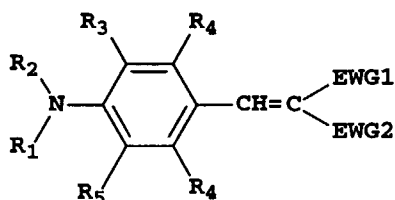
the spectral absorbance maximum of the density correction dye is in the range of 450-485 nm;
the ratio of the absorbance of the density correction dye at 480 nm relative to 420 nm is between 1.2 and 3.5;
the ratio of the absorbance of the density correction dye at 440 nm relative to 420 nm is between 1.25 and 2.5;
the ratio of the absorbance of the density correction dye at 510 nm relative to 480 nm is less than 0.6; and
the dye is free of charged groups, carboxyl groups, and sulfonate groups.

2. A color negative element according to claim 1, wherein the log P of the density correction dye or dyes calculated by Medchem version 3.54 is at least 4.0.

3. A color negative element according to claim 1, wherein:

the density correction dye has an absorbance maximum between 455 and 480 nm;
the ratio of absorbance at 480 nm relative to 420 nm is between 1.3 and 3.0;
the ratio of absorbance at 440 nm relative to 420 nm is between 1.35 and 2.2; and
the ratio of absorbance at 510 nm relative to 480 nm is less than or equal to 0.55.

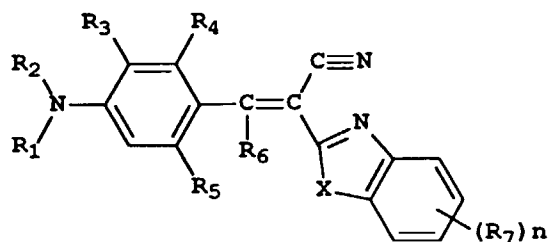
4. A color negative element according to claims 1 to 3, wherein the yellow or orange-yellow density correction dye is of structure I, below



wherein:

R₁ is hydrogen or an alkyl group;
R₂ is an alkyl group or an aryl group;
R₃ is hydrogen, an alkyl group, an alkoxy group or an aryloxy group;
R₄ is hydrogen, an alkyl group or an alkoxy group;
R₅ is hydrogen or an alkyl group;
R₁ and R₂, R₂ and R₃ or R₁ and R₅ may join to form a ring; and
EWG1 and EWG2 are electron-withdrawing groups.

5. A color negative element according to claim 4, wherein EWG1 is a cyano group.
6. A multilayer color negative photographic element according to claims 1-5 when the yellow or orange-yellow density correction dye is of structure III,



III

wherein:

R₁ is hydrogen or an alkyl group;

R₂ is an alkyl group or an aryl group;

R₃ is hydrogen, a halogen atom, an alkyl group, an alkoxy group or an aryloxy group;

R₄ is hydrogen or an alkyl group;

R₅ is hydrogen or an alkyl group;

R₆ is hydrogen or an alkyl group;

X is oxygen or sulfur;

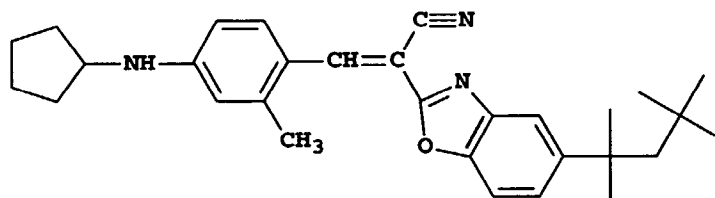
each R₇ is independently a substituent selected from the group consisting of a halogen atom, and alkyl, aryl, alkoxy, aryloxy, carbonamido, sulfonamido, carbamoyl, alkoxycarbonyl, aryloxycarbonyl and acyloxy, acyl, sulfamoyl, sulfonyl, sulfoxyl, alkylthio, arylthio and cyano groups;

n is 0, 1, 2 or 3; and

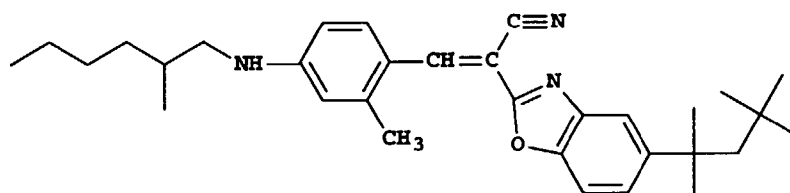
R₁ and R₂ or R₂ and R₃ may join to form a ring.

7. A color negative element according to claim 6, wherein R₁ is hydrogen, R₂ is alkyl, R₃ is hydrogen or alkyl, R₄ is hydrogen, R₅ is alkyl, R₆ is hydrogen, X is oxygen, n is 0 or 1 and, when n is 1, R₇ is an alkyl group, a sulfonamido group or a halogen in the para position relative to X.

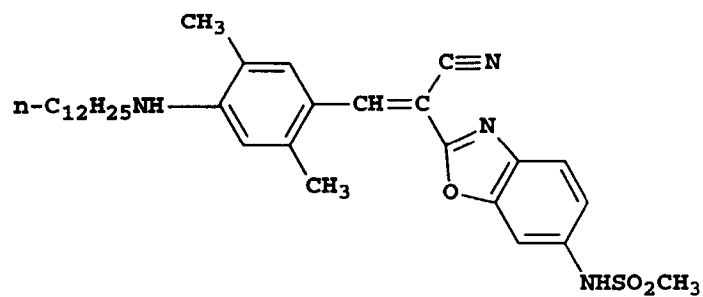
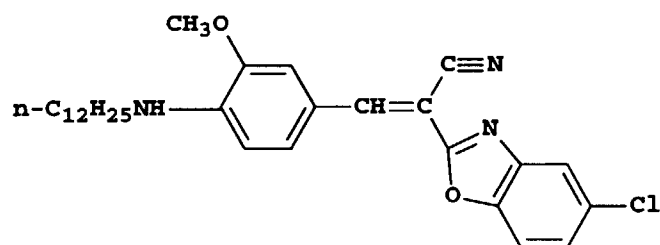
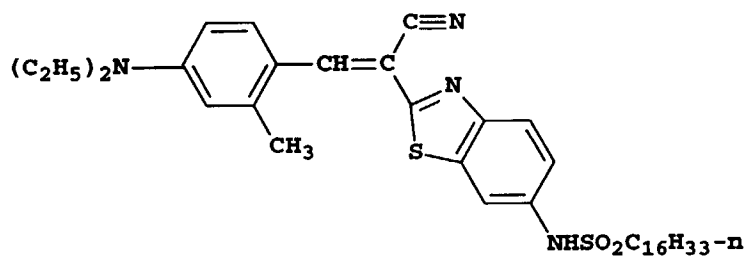
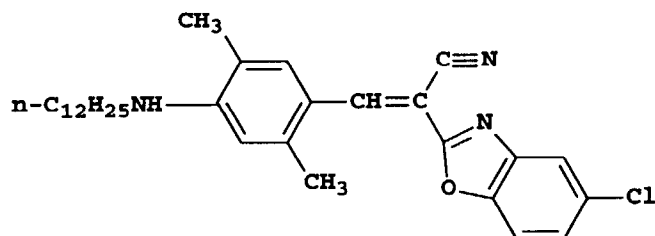
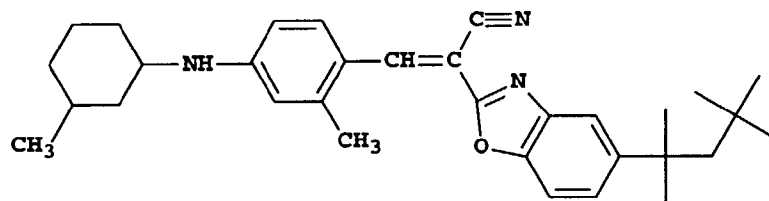
8. A color negative element according to claims 1-7, wherein the methine density correction dye is selected from the group consisting of the following:

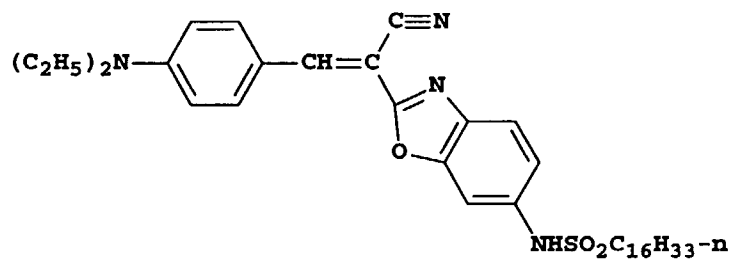
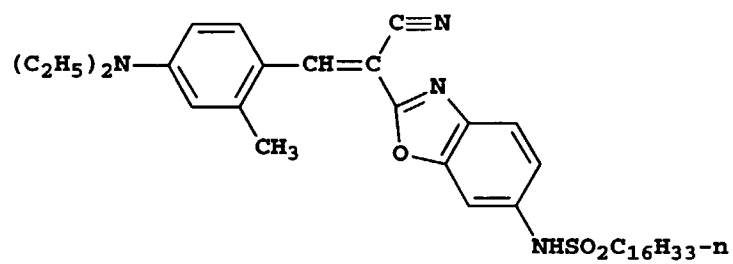
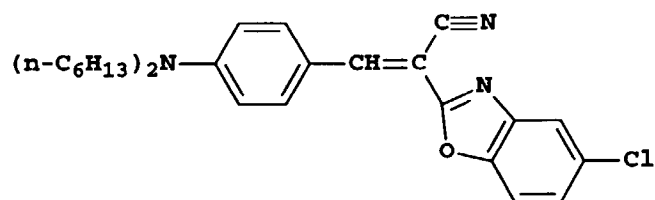
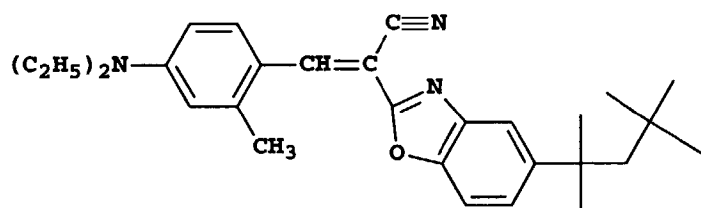
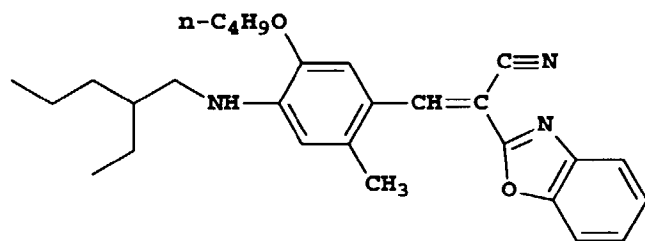


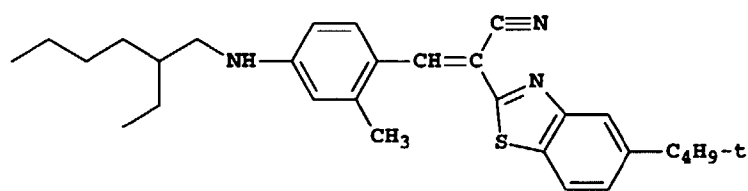
DA1



DA2

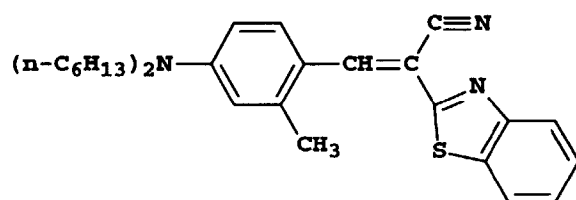






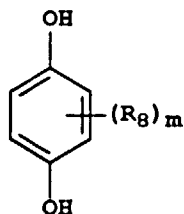
DA29

and

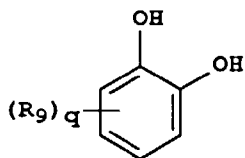


DA30

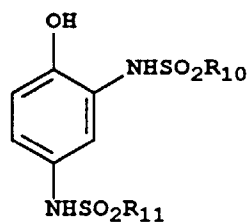
9. The element of claims 6-8 wherein dyes of structure III is codispersed with one or more hydroquinone, catechol or sulfonamidophenol reducing agents.
10. A color negative photographic element according to claim 9, wherein the hydroquinone, catechol and sulfonamidophenol reducing agents are of structures IV, V and VI, respectively,



IV



V



VI

wherein:

each R_8 is an independently selected from the group consisting of an alkyl group, a carbonamido group, a carbamoyl group, an alkoxy group, an aryloxy group and a chlorine atom, and m is 1 to 4;

each R_9 is independently selected from the group consisting of an alkyl group, a carbonamido group, a carbamoyl group, an alkoxy group, an aryloxy group and a chlorine atom, and q is 1 to 4;

R_{10} is an aryl group or an alkyl group; and

R_{11} is an aryl group or an alkyl group.