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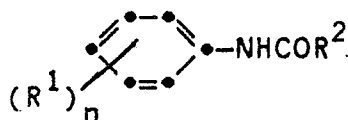
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54 Photographic recording material comprising a dye image-forming compound.

57 This invention relates to a color photographic silver halide recording material containing certain dye image-forming coupler compounds and a carbonamide compound



wherein;

R¹ is a substituted or unsubstituted alkyl or an electron withdrawing group;

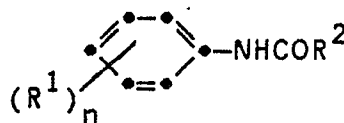
R² is a substituted or unsubstituted aryl group or a substituted or unsubstituted alkyl group which is free of carboxylic group substitution; and

n is 0 to 3 which is capable of altering the spectral absorption properties of a dye formed by reaction of the coupler compound with oxidized developing agent.

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n is 0 to 3.

This invention also relates to a color photographic record comprising a dye formed by a coupling reaction between a dye forming coupler and oxidized silver halide developing agent, which record comprises, in association with the dye, a carbonamide compound having the structural formula:



wherein;

R¹ is a substituted or unsubstituted alkyl or an electron withdrawing group;

R² is a substituted or unsubstituted aryl group or a substituted or unsubstituted alkyl group which is free of carboxylic group substitution; and

n is 0 to 3.

Electron-withdrawing groups represented by R¹ include -CN, -NO₂, a halogen atom,

- C(=O)NHR³,

- C(=O)R³

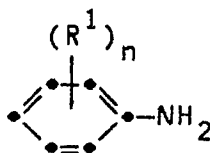
and -SO₂R³,

where R³ is a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group.

The alkyl groups which can be represented by R¹, R² or R³ can have from 1 to about 20 carbon atoms. Preferred alkyl groups have from 1 to about 12 carbon atoms. Such groups can be straight or branched chain and can be substituted. The aryl groups which can be represented by R² or R³ can have from about 6 to about 12 carbon atoms and can be substituted.

Substituents which can be present on the R¹, R² and R³ groups include other alkyl groups having the 1 to 6 carbon atoms, and halogen atoms. Chlorine is a preferred halogen substituent, particularly on an aryl ring inasmuch as it provides good stability properties and is least expensive to manufacture.

The described carbonamide compounds can be synthesized by reacting an aliphatic or an aromatic acid chloride compound having the formula R²COCl with a primary aromatic amine compound of the formula:



where R¹, R², R³ and n have the meanings as described above, according to procedures known in the chemical art.

There are no particular restrictions on the quantity of carbonamide compound which can be employed with a dye image-forming compound either alone or when combined with known coupler solvents.

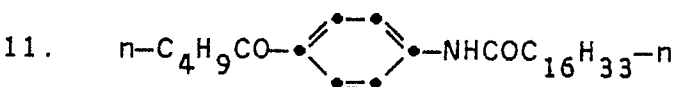
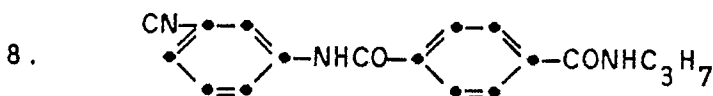
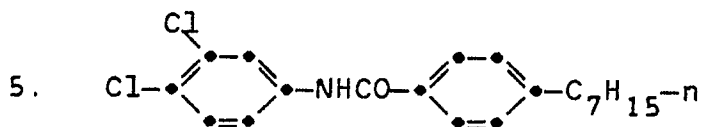
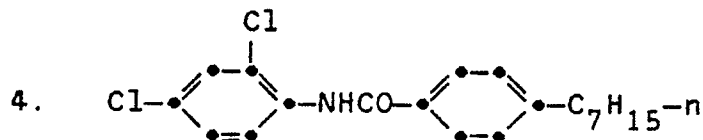
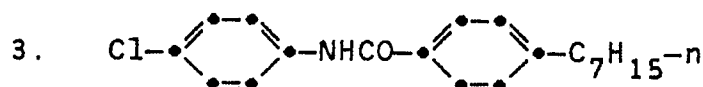
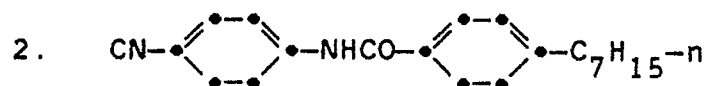
Generally, it is desirable that the quantity of carbonamide compound, with respect to each part by weight of the coupler, be from about 0.05 to about 10 parts, preferably from about 0.2 to about 3 parts by weight of the coupler compound. As the amount of carbonamide compound increases, relative to the amount of coupler compound employed, there is usually a detectable increase in the extent of hue shift in the image dye. However, the particular choice of coupler, of carbonamide compound or the presence of one or more coupler solvents, all tend to influence the type and the extent of spectral absorption change in the resulting image dye.

Two or more carbonamide compounds may be used in combination to alter the spectral absorption properties of dyes as described herein.

When the coupler compound is added to a silver halide emulsion, conventional procedures may be employed. For example, the coupler can first be dissolved in one or more known coupler solvents, such as di-n-butyl phthalate (DBP), and then be mixed with a carbonamide compound as described herein. If desired, the coupler compound can be mixed with a carbonamide compound where these compounds are

sufficiently compatible, so that known coupler solvents may not be needed. The resulting mixture or solution is then dispersed in aqueous gelatin, preferably containing a surfactant, and the dispersion is added to a silver halide emulsion which can then be coated by known techniques.

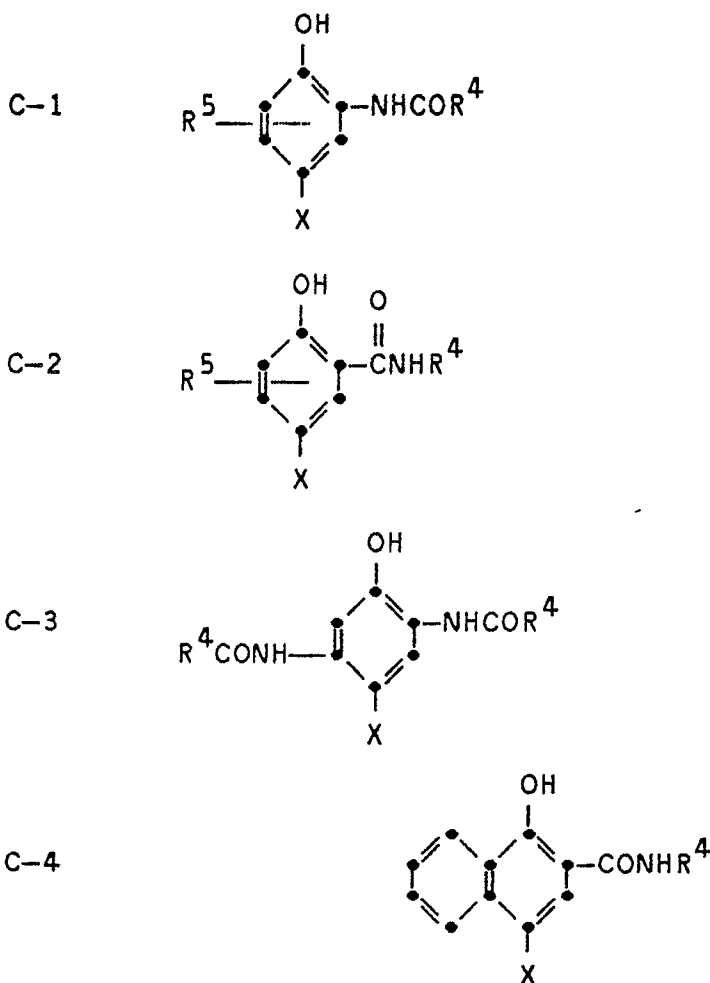
Preferred carbonamide compounds which are useful for shifting absorption values of dyes, including dyes obtained by the reaction of dye image-forming coupler compounds with oxidized color developing agents, include the following:



Couplers which form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as U.S. Patent Nos. 2,474,293; 2,772,162; 2,801,171; 2,895,826; 3,002,836; 3,419,390; 3,476,563; 3,779,763; 3,996,253; 4,124,396; 4,248,962; 4,254,212;

4,296,200; 4,333,999; 4,443,536; 4,457,559; 4,500,635; and 4,526,864, the disclosures of which are incorporated herein by reference.

Preferred cyan coupler structures are phenols and naphthols which form cyan dyes on reaction with oxidized color developing agent. These preferred structures include the following moieties:



40 where R^4 represents a ballast group, R^5 represents one or more halogen atoms (e.g., chloro, fluoro), lower alkyl (e.g., methyl, ethyl, butyl) or lower alkoxy (e.g., methoxy, ethoxy, butoxy) groups and X is hydrogen or a coupling off group.

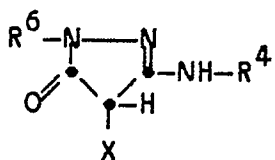
An especially preferred R^4 on a C-3 type coupler structure is the group



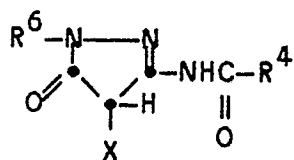
such as is described in US Patent 4,333,999.

50 Magenta dye image-forming couplers, which are not aldehydebis 5-pyrazolone or pyrazolino-[1,5-a]-benzimidazole magenta type couplers, which form magenta dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Patent Nos. 1,969,479; 2,311,082; 2,343,703; 2,369,489; 2,600,788; 2,908,573; 3,061,432; 3,062,653; 3,152,896; 3,519,429; 3,725,067; 4,120,723; 4,500,630; 4,540,654 and 4,581,326; and European Patent Publication Nos. 170,164 and 177,765; and copending U.S. Application Serial Numbers 23,517 of S. Normandin et al; 23,518 of R. Romanet et al; 23,519 of A. Bowne et al and 23,520 of A. Bowne et al, all filed March 9, 1987, the disclosures of which are incorporated herein by reference.

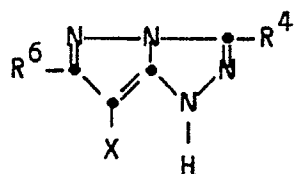
55 Preferred magenta couplers include pyrazolones compounds having the structural formulae:



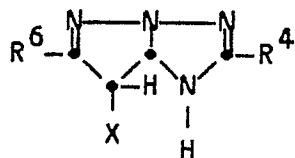
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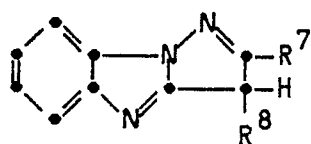
pyrazolotriazole compounds having the structural formulae:



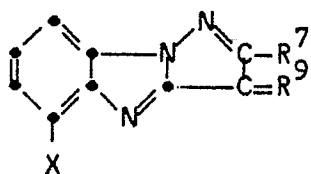
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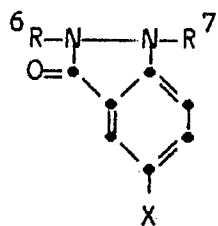
pyrazolobenzimidazole compounds having the structural formulae:



and



and indazole compounds having the structural formula:



wherein

X is as defined above;

R⁴ is a ballast group;R⁶ is halogen (e.g., chloro, fluoro), alkyl or alkoxy having from 1 to 4 carbon atoms, phenyl or substituted

phenyl (e.g., 2,4,6-trihalophenyl);

R⁷ is hydrogen or a monovalent organic radical, for example a saturated or unsaturated alkyl group having from 1 to about 20 carbon atoms (methyl, ethyl, propyl, butyl, decyl, dodecyl, heptadecyl, octadecyl); a cycloalkyl group (e.g. cyclohexyl); an aralkyl group (e.g. benzyl); an aryl group (e.g. phenyl, alkoxyphenyl in which the alkyl or alkoxy radical has from 1 to about 20 carbon atoms, nitrophenyl, aminophenyl, acylaminophenyl, alkylaminophenyl, naphthyl, diphenyl, diphenylether, diphenylthioether); a heterocyclic group (e.g. a-furyl, a-benzofuryl, a-pyridyl); an amino, hydroxy or carboxylic acid group, it being possible for the hydrogen atoms of these groups to be substituted, for instance by a mono- or dialkylamino group in which the alkyl groups have from 1 to about 20 carbon atoms; a cycloalkylamino group; an amino group in which one hydrogen atom is replaced by a pyrazolo-[1,5-a]-benzimidazolyl radical which is bonded in 3-position to said nitrogen atom so that couplers result in which two pyrazolo-[1,5-a]-benzimidazolyl radicals are connected by an amino group, and in which the remaining hydrogen atom may be replaced by a substituent such as an alkyl-, aryl-, aralkyl- or acyl- radical; an acylamino group in which the acyl radical is derived from an aliphatic, aromatic or heterocyclic carboxylic acid; a carboxylic acid group which is esterified by means of an aliphatic, cycloaliphatic or aromatic alcohol or by an aromatic compound having a phenolic hydroxy group; or a carboxyamido group in which the amido group may be substituted for example by a saturated or unsaturated alkyl, aralkyl, aryl or heterocyclic group;

R⁸ represents a hydrogen atom, a sulphonic acid or a carboxylic acid group; a halogen atom (e.g. chlorine or bromine); or an azo radical -N=NR¹³, wherein R¹³ can be an aromatic or heterocyclic radical (phenyl, naphthyl, diphenyl, diphenylether, benzthiazolyl, pyridyl, quinolyl or pyrazolyl) which may be substituted such as by an alkyl group having from 1 to about 20 carbon atoms, hydroxy, alkoxy, halogen, amino, substituted amino, nitro, sulphonic acid or carboxylic acid groups;

R⁹ represents a divalent radical such as

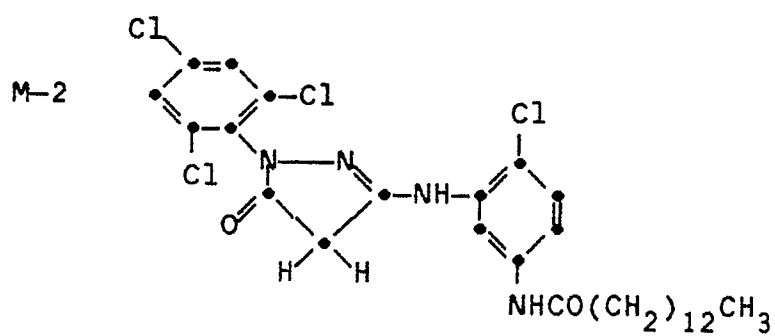
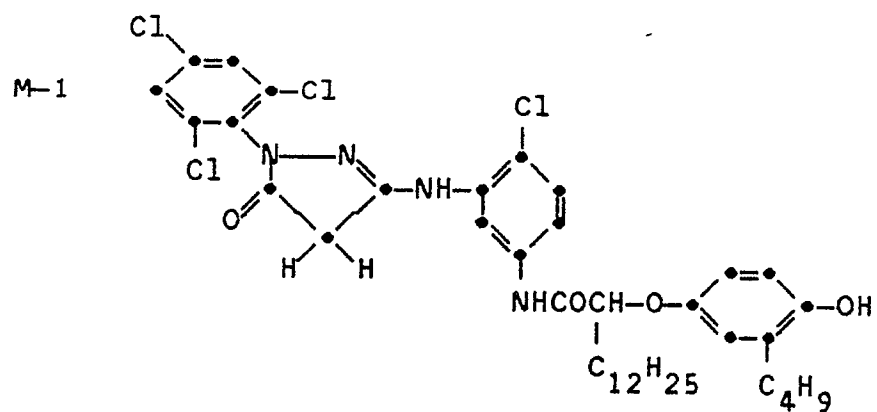


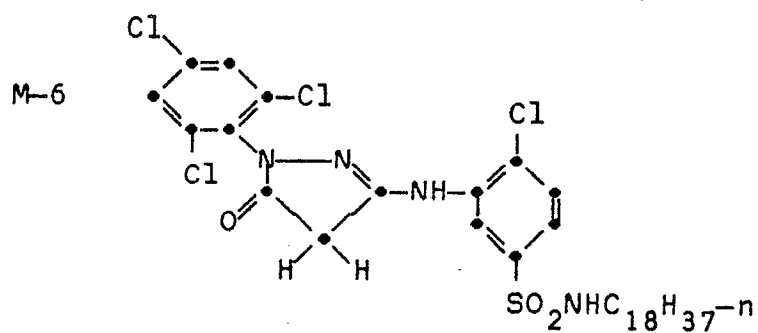
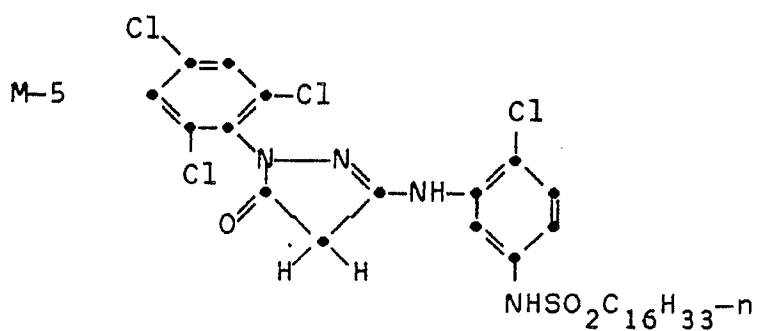
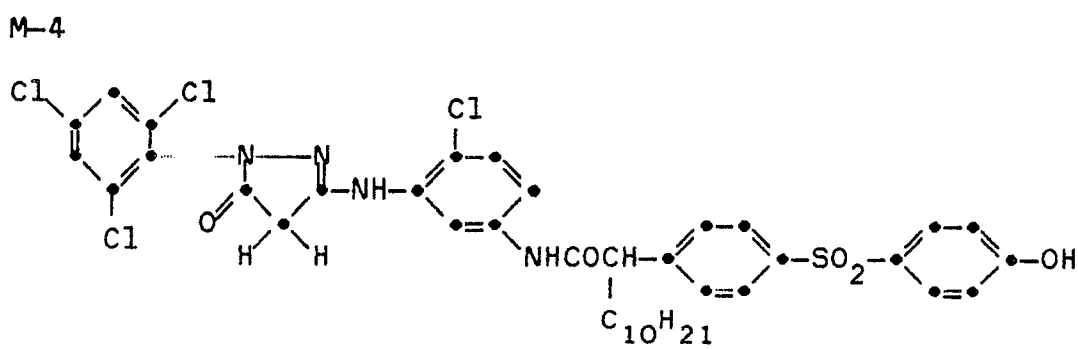
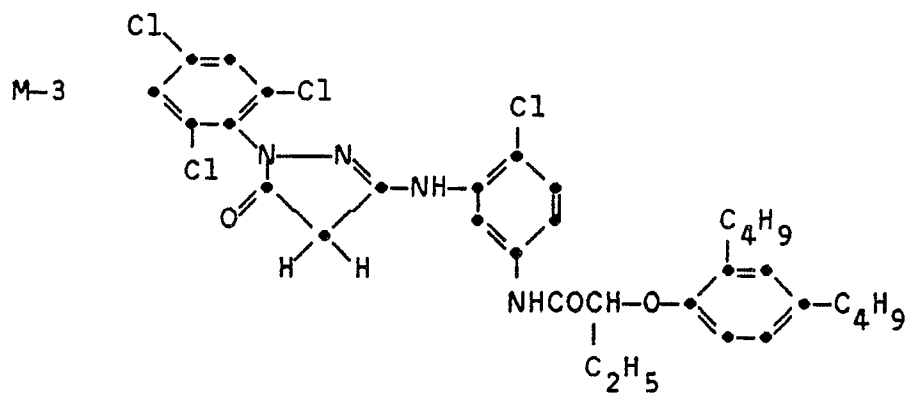
wherein R¹⁰ can be alkyl, aralkyl, especially phenyl, phenyl substituted preferably in the p-position by a tertiary amino group such as a dialkylamino group in which at least one of the alkyl groups is substituted by carboxy, sulpho, hydroxy, alkoxy, carboxylalkyl, cyano or the divalent radical



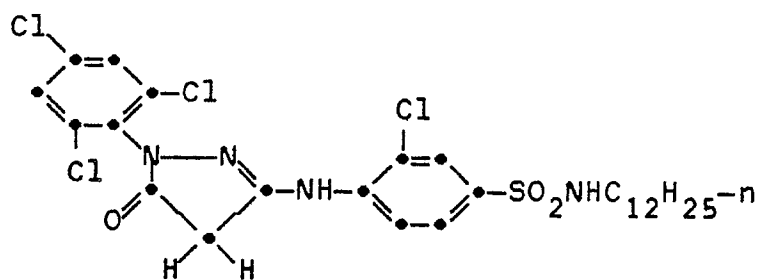
wherein R¹¹ and R¹² represent aliphatic, aromatic, araliphatic or heterocyclic radicals.

Specific magenta dye forming coupler compounds which are useful in the practice of this invention include:

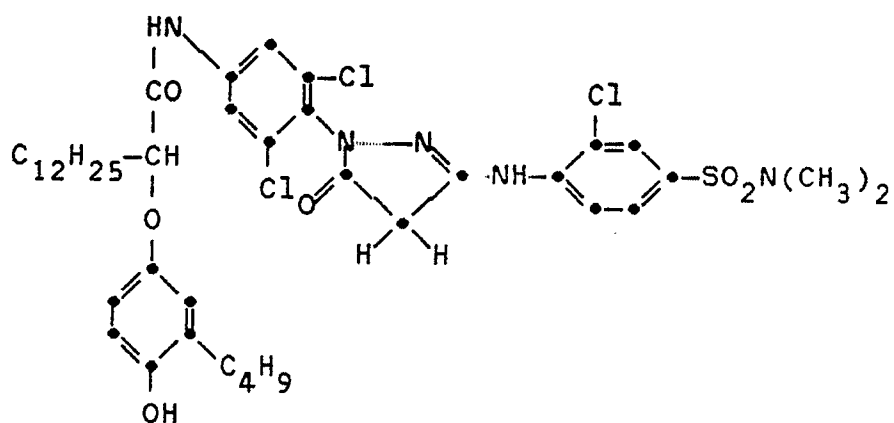




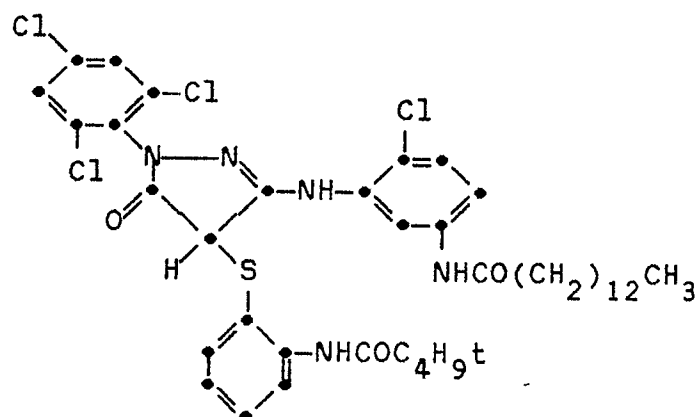
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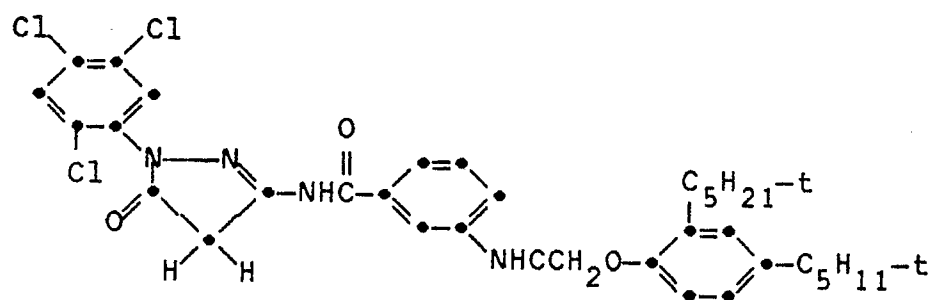
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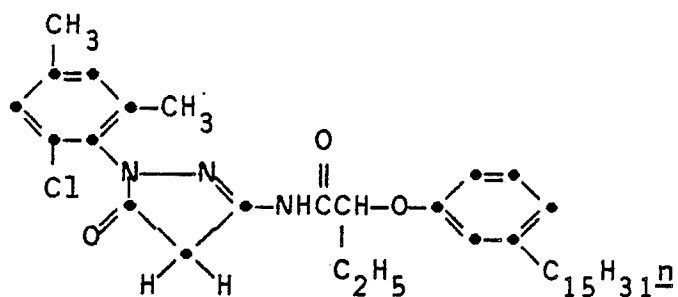
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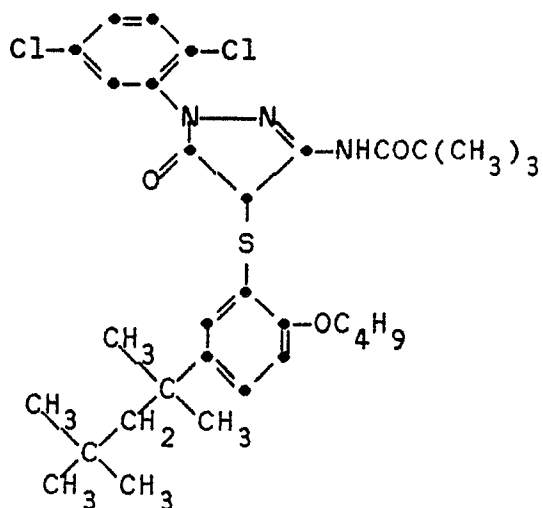
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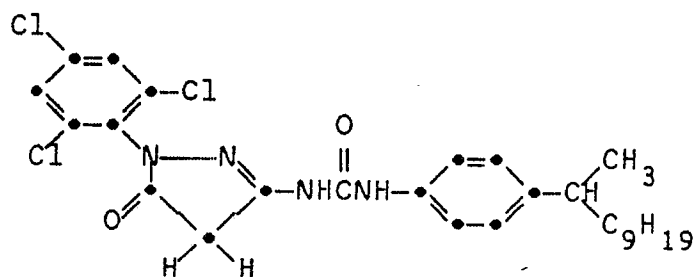
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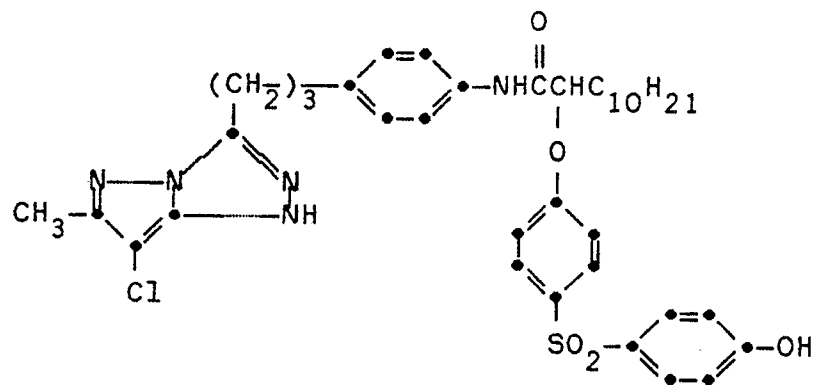
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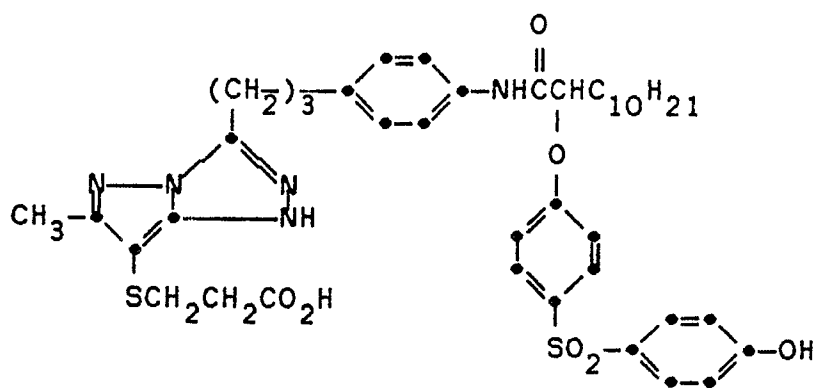
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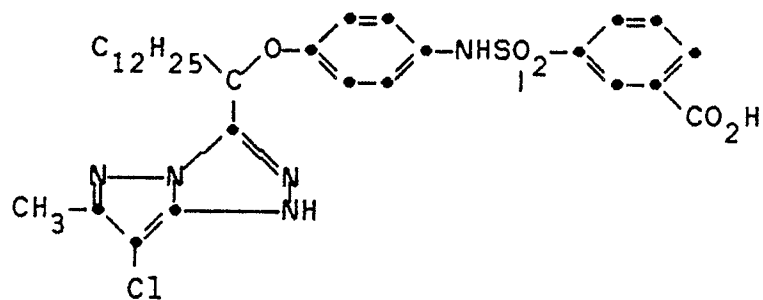
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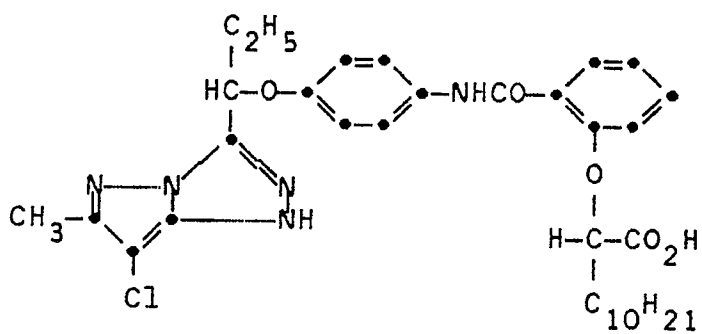
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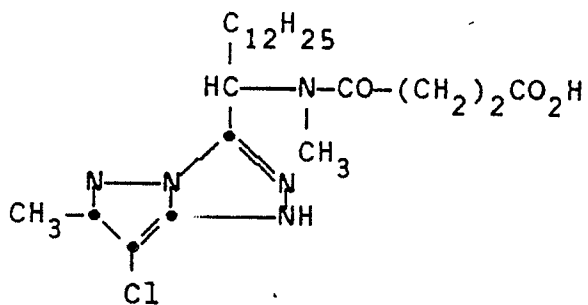
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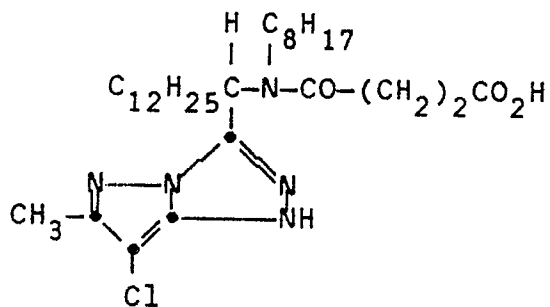
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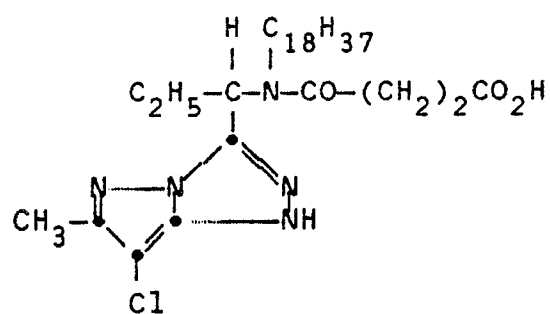
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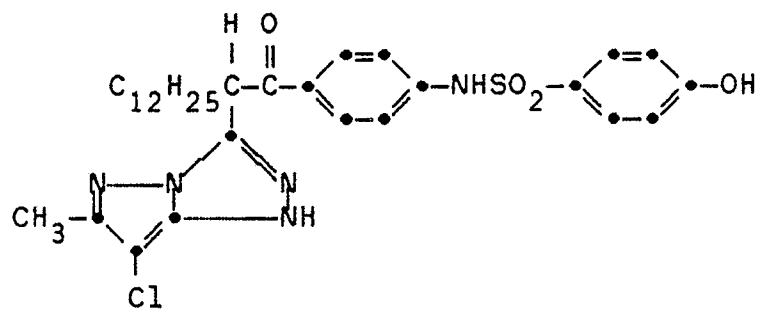
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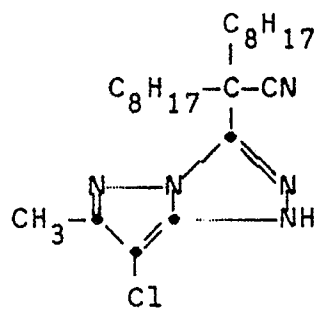
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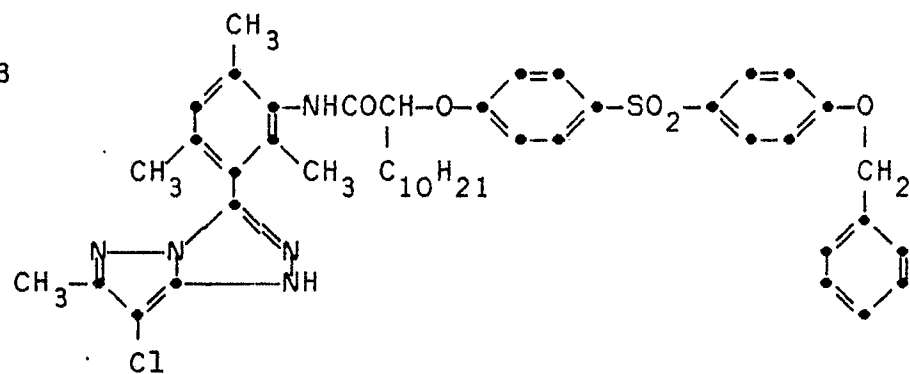
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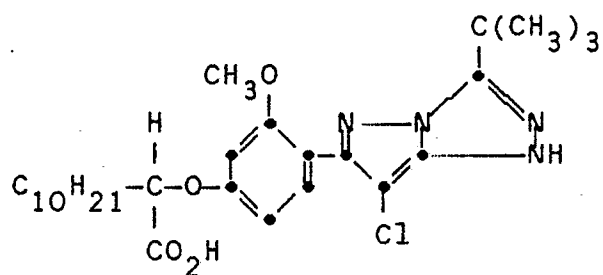
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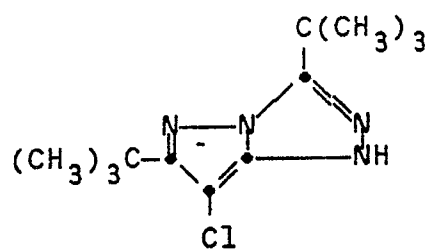
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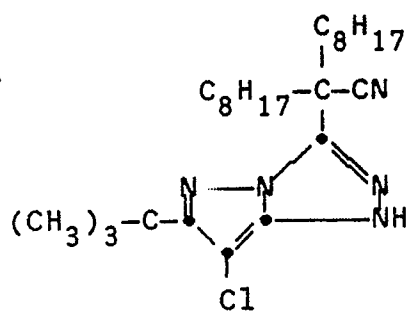
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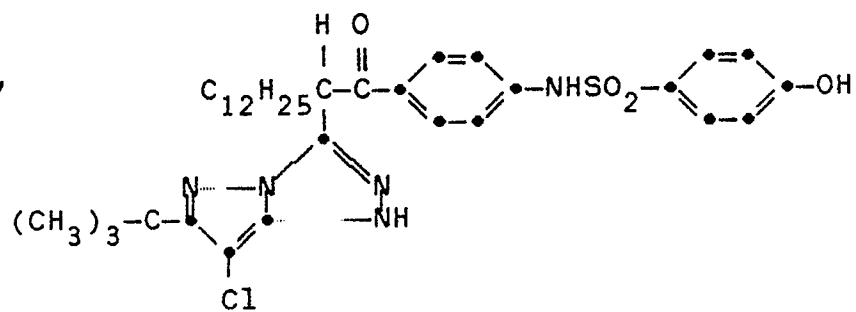
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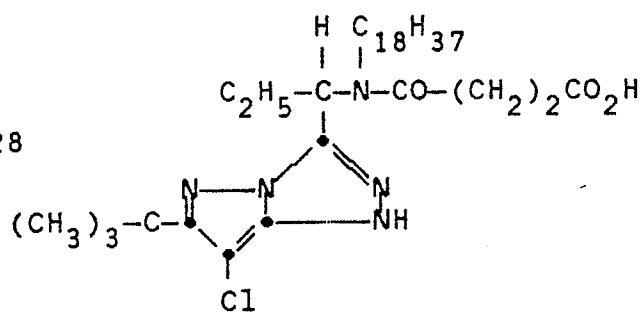
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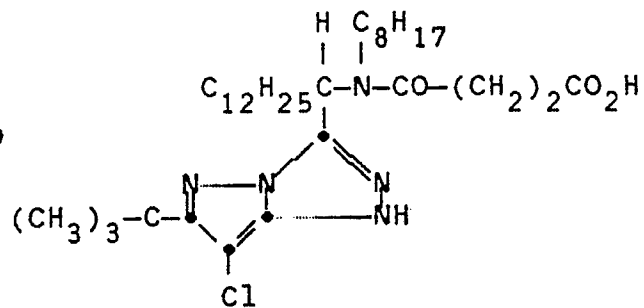
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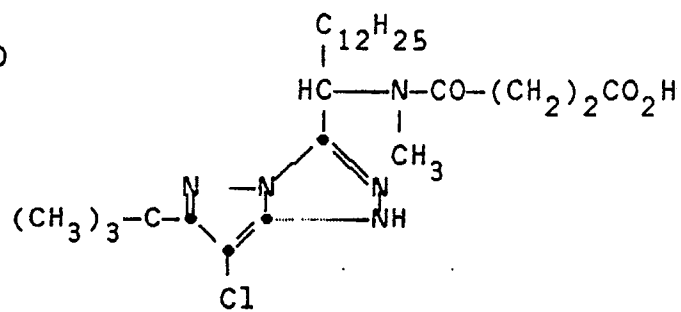
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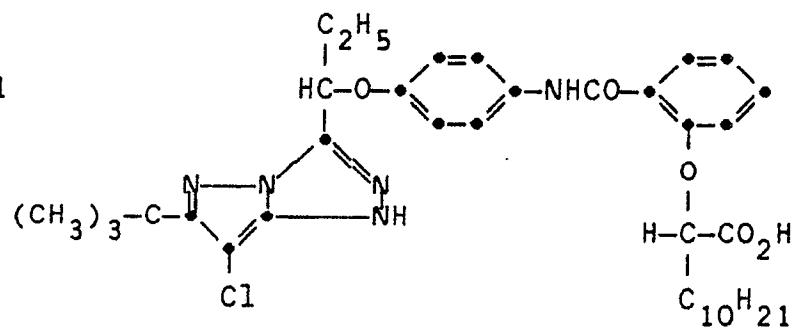
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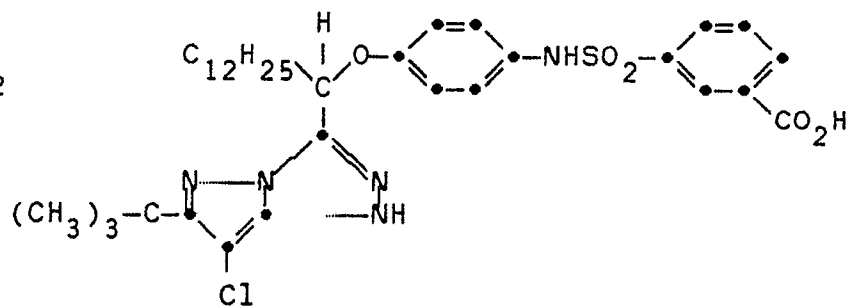
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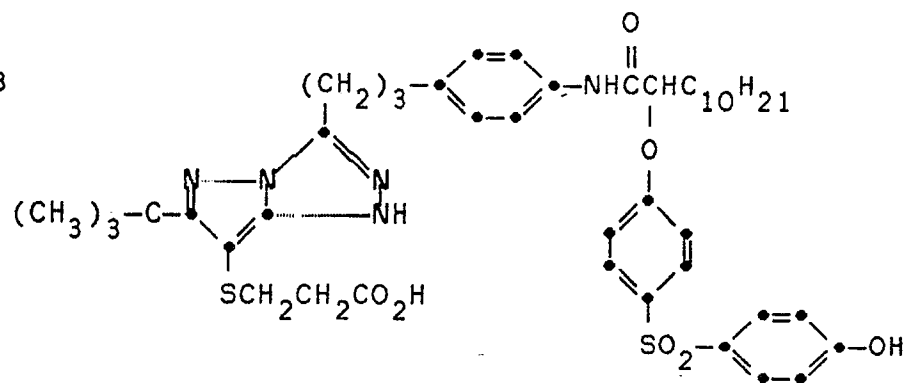
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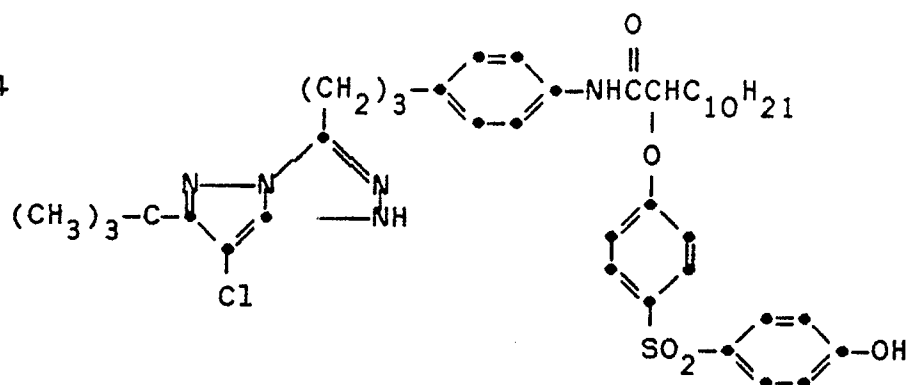
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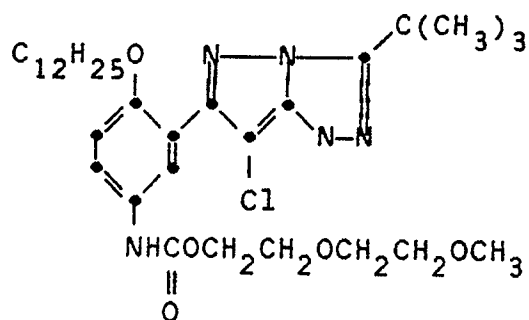
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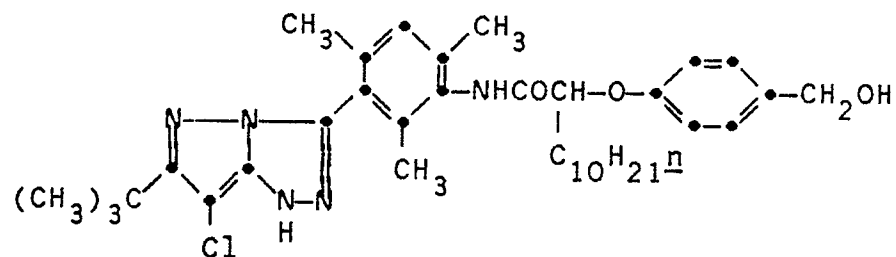
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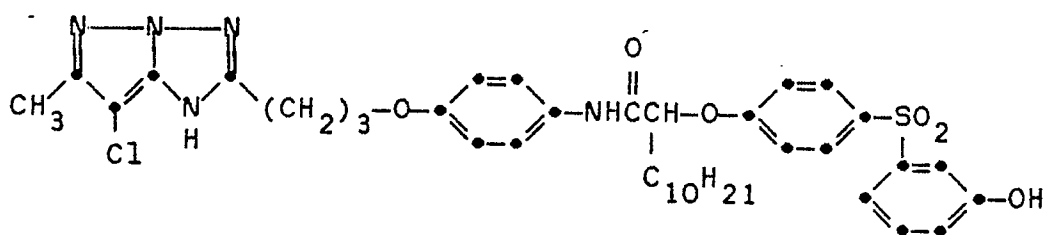
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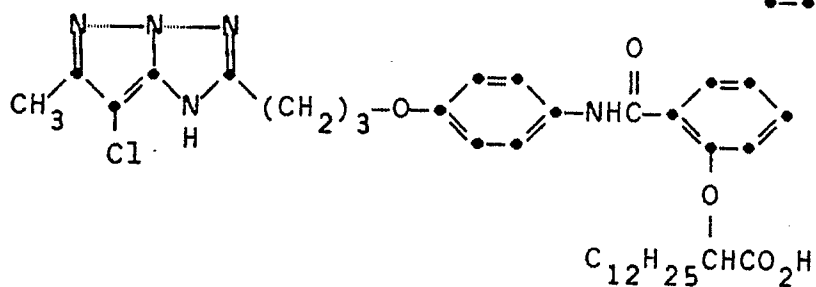
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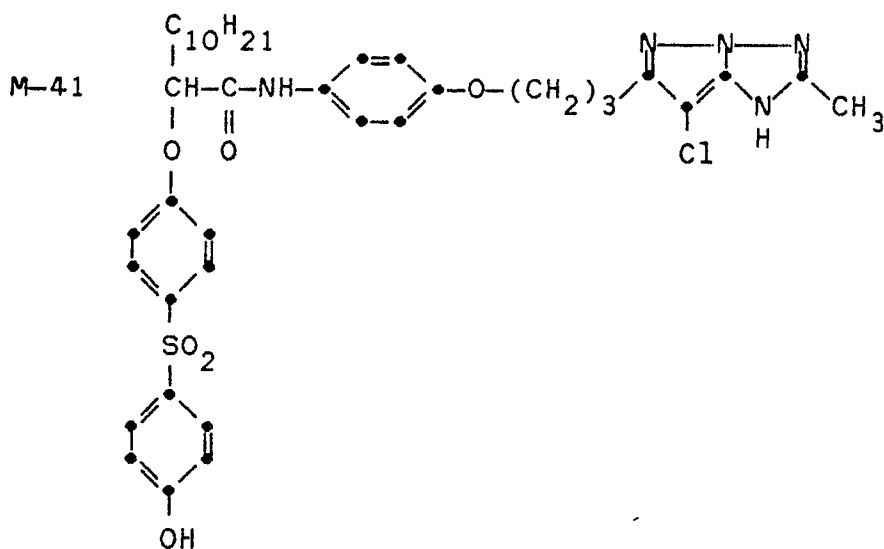
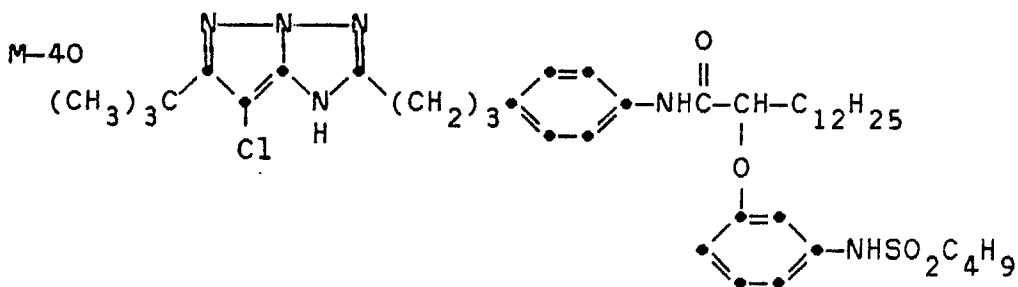
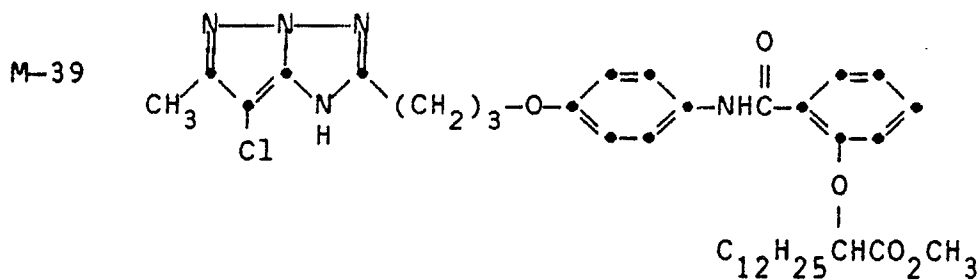


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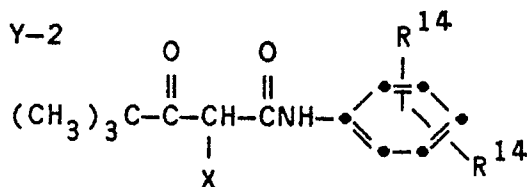
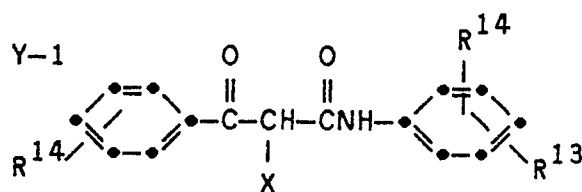
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Couplers which form yellow dyes upon reaction with oxidized color developing agent are described in such representative U. S. Patents as Nos. 2,298,443; 2,875,057; 2,407,210; 3,265,506; 3,384,657; 3,408,194; 3,415,652; 3,447,928; 3,542,840; 4,046,575; 3,894,875; 4,095,983; 4,182,630; 4,203,768; 4,221,860; 4,326,024; 4,401,752; 4,443,536; 4,529,691; 4,587,205; 4,587,207 and 4,617,256 the disclosures of which are incorporated herein by reference.

Preferred yellow dye image-forming couplers are acylacetamides, such as, benzoylacetanilides and pivalylacetanilides. Structures of such preferred coupler moieties are:



where R¹³ is as defined above R¹⁴ is hydrogen or one or more halogen, lower alkyl (e.g. methyl, ethyl) or a ballast (e.g. alkoxy of 16 to 20 carbon atoms) group and X is a coupling off group.

Photographic elements in which the photographic couplers of this invention are incorporated can be simple elements comprising a support and a single silver halide emulsion layer, or they can be multilayer, multicolor elements. The coupler compounds of this invention can be incorporated in the silver halide emulsion layer or in another layer, such as adjacent layer, where they will come into reactive association with oxidized color developing agent which has developed silver halide in the emulsion layer. The silver halide emulsion layer can contain, or have associated therewith, other photographic coupler compounds, such as color forming couplers, colored masking couplers, etc. These other photographic coupler compounds can form dyes of the same or different color and hue as the photographic coupler compounds of this invention. Additionally, the silver halide emulsion layer can contain addenda conventionally contained in such layers.

A typical multilayer, multicolor photographic element according to this invention comprises a support having thereon a red-sensitive silver halide emulsion layer having associated therewith a cyan dye image-forming coupler compound, a green-sensitive silver halide emulsion layer having associated therewith a magenta dye image-forming coupler compound and a blue-sensitive silver halide emulsion layer having associated therewith a yellow dye image-forming coupler compound, wherein at least one dye image-forming coupler compound has associated therewith a carbonamide compound as described herein. Each silver halide emulsion layer can be composed of one or more layers and the layers can be arranged in different locations with respect to one another. Typical arrangements are described in U.S. Patent Nos. 3,227,554; 3,620,747; 3,843,369; and 4,400,463 and in U.S. Patent No. 923,045.

The light sensitive silver halide emulsions can include coarse, regular or fine grain silver halide crystals or mixtures thereof and can be comprised of such silver halides as silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide and mixtures thereof. The emulsions can be negative-working or direc-positive emulsions. They can form latent images predominantly on the surface of the silver halide grains or predominantly on the interior of the silver halide grains. They can be chemically and spectrally sensitized. The emulsions typically will be gelatin emulsions although other hydrophilic colloids can be used in accordance with usual practice.

The support can be of any suitable material used with photographic elements. Typically, a flexible support is employed, such as a polymeric film or paper support. Such supports include cellulose nitrate, cellulose acetate, polyvinylacetal, polyethylene terephthalate, polycarbonate and resinous materials as well as glass, paper or metal. Paper supports can be acetylated or coated with baryta and/or an a-olefin polymer, particularly a polymer of an a-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene or ethylene-butene copolymers.

Further details regarding silver halide emulsions and elements, and addenda incorporated therein can be found in Research Disclosure, December 1971, Item 9232, Paragraphs I through XVIII. Research Disclosure is published by Industrial Opportunities Ltd., Homewell, Havant, Hampshire, PO9 1EF, United Kingdom.

The term "in association" and "associated with" are intended to mean that materials can be in either the same or different layers so long as the materials are accessible to one another.

Example 1 Hue shifting of preformed dyes

Dyes were dissolved in the coupler solvent, di-n-butyl phthalate (DBP), with or without a carbonamide compound, and coated in a gelatin vehicle in single layers.

5 A solution of 10ml (12.5% solution) of photographic grade gelatin and 10 ml (0.4% aqueous solution) of duPont Alkanol XC were added to each solution of dye as described below. The indicated weight ratio of carbonamide compound dissolved in 1 ml of ethyl acetate was then added.

This mixture was passed five times through a colloid mill and 0.2 ml (10% solution) Olin Corp. 10G surfactant and 0.05 ml (5% solution) formaldehyde were added. The milled mixture was then coated on a
10 poly(ethyleneterephthalate) support, 100 mm wet thickness, and dried at 49° C. After 24 hours, the coating was washed for 5 minutes, dried, and spectrophotometric absorption maxima values were obtained.

The following Table shows that carbonamide compounds as described herein are capable of shifting the absorption maxima of dyes to usefully longer wavelengths. As these dyes are preformed and avoid wet processing, this experiment indicates the concept of hue shifting is applicable to other than photographic
15 systems. The extent of hue shifting depends upon the specific dye and carbonamide compound (CC) and also varies with the dye:carbonamide compound ratio. The Table reflects the Dye:DBP:(CC) ratio used in each test.

Table

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Dye Compound	Carbonamide Compound	Weight Ratio Dye:DBP:(CC)	g-max, nm
A	none (control)	1 : 3 : 0	532
A	1	1 : 2 : 1	536
A	2	1 : 2 : 1	537
B	none (control)	1 : 3 : 0	533
B	1	1 : 2 : 1	549
C	none (control)	1 : 3 : 0	639
C	1	1 : 2 : 1	649
C	2	1 : 2 : 1	651

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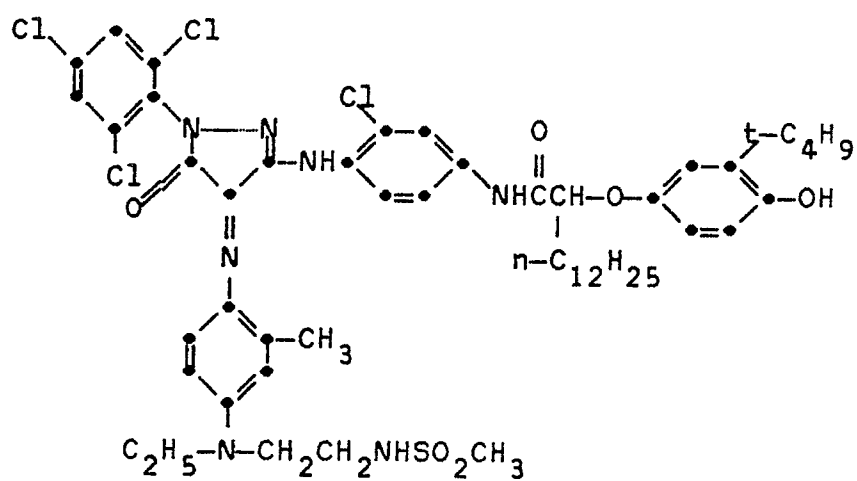
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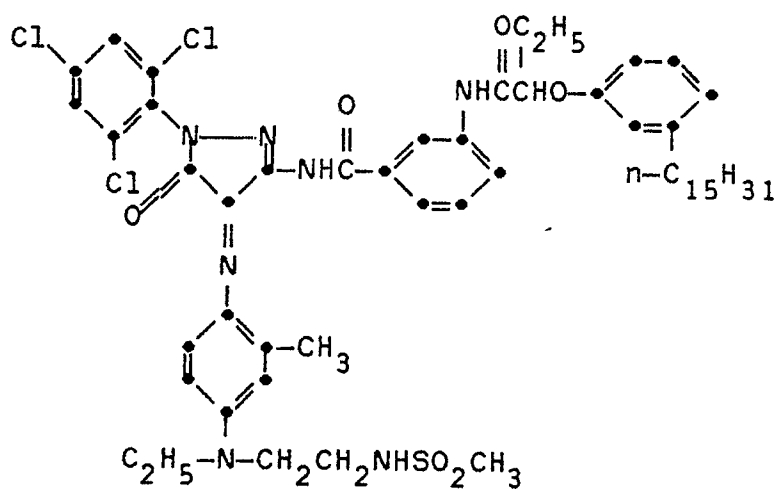
As is demonstrated by the data in the Table hue shifts to longer wavelengths vary from only a few nanometers to as much as 16 nanometers depending upon the dye and the carbonamide compound used. These variations in wavelength shifts offer a high degree of manipulative control and provide an excellent, inexpensive means to obtain particularly desired hue values with a variety of dye types.

Dye Structures:

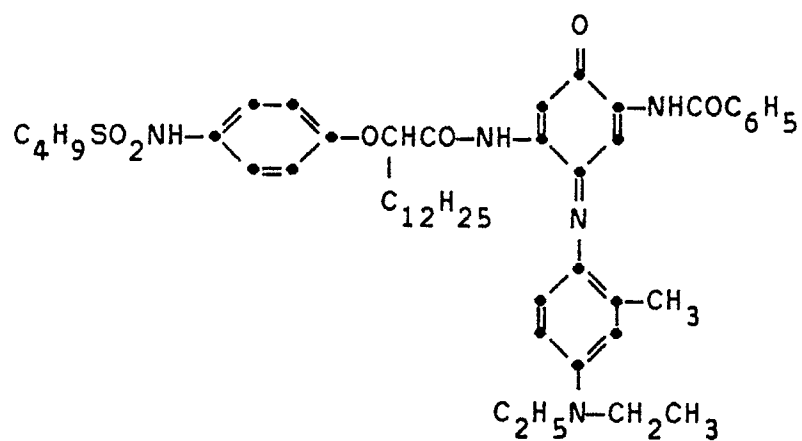
A



B

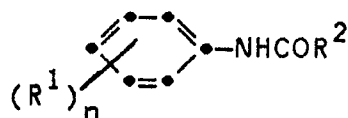


C



Claims

1. A color photographic recording material comprising a support having thereon a light-sensitive silver halide emulsion layer, a coupler compound which is (i) a yellow or a cyan dye image-forming coupler or (ii) a magenta dye image-forming coupler, which is not an aldehydebis type 5-pyrazolone or a pyrazolino-[1,5-a]-benzimidazole magenta coupler, which coupler is capable of forming a dye by reaction with oxidized color developing agent and, associated with the coupler, a carbonamide compound which is capable of altering spectral absorption of a dye formed from the coupler, said carbonamide compound having the structural formula:



wherein;

R¹ is a substituted or unsubstituted alkyl or an electron withdrawing group;

R² is a substituted or unsubstituted aryl group or a substituted or unsubstituted alkyl group which is free of carboxylic group substitution; and

n is 0 to 3.

2. A photographic recording material according to claim 1 wherein R¹ is an electron withdrawing group which is -CN, -NO₂, a halogen atom - $\text{C}(=\text{O})\text{NHR}^3$,



or -SO₂R³,

wherein R³ is a substituted or unsubstituted alkyl or a substituted or unsubstituted aryl group having from 6 to 12 carbon atoms.

3. A photographic recording material according to claim 2 wherein R¹ is chloro.

4. A photographic recording material according to any of claims 1 to 3 wherein R³ is an alkyl group having from 1 to 12 carbon atoms.

5. a photographic recording material according to any of claims 1 to 4 wherein R² is an alkyl group having from 1 to 20 carbon atoms or an aryl group having from 6 to 12 carbon atoms.

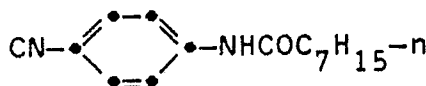
6. A photographic recording material according to claim 5 wherein R² is an alkyl group having from 1 to 12 carbon atoms.

7. A photographic recording material according to claim 5 wherein R² is a substituted or unsubstituted phenyl group.

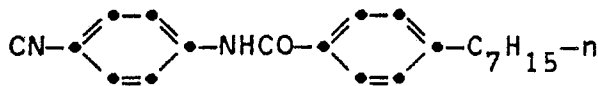
8. A photographic recording material according to claim 7 wherein the phenyl group is substituted with an alkyl group having from 1 to 20 carbon atoms.

9. A photographic recording material according to any of claims 1 to 8 wherein the carbonamide compound is present in an amount of from 0.05 to 10, preferably from 0.2 to 3, parts by weight of coupler compound.

10. A photographic recording material according to claim 1 or 9 wherein the carbonamide compound has the structural formula:



or



11. A photographic recording material according to any of claims 1 to 10 wherein the dye image-forming coupler is a cyan or magenta coupler compound.

12. A photographic recording material according to any of claims 1 to 11 wherein the dye is formed from a pyrazolone, pyrazolotriazole, pyrazolobenzimidazole or indazole magenta coupler compound.

5 13. A color photographic record comprising a dye formed by a coupling reaction between a dye forming coupler and oxidized silver halide developing agent, which record comprises, in association with the dye, a carbonamide compound as specified in any of claims 1 to 12.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 8570

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
P,X	EP-A-0 268 496 (KONICA) * Formula A-55; claims * ---	1-13	G 03 C 7/26 G 03 C 7/38
A,D	GB-A-1 076 054 (ILFORD) * Whole document * -----	1-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			G 03 C 7/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-11-1988	Examiner MAGRIZOS S.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			