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

(11) Publication number: **0 012 020**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **79302730.1**

(22) Date of filing: **29.11.79**

(51) Int. Cl.³: **G 03 C 1/84**
G 03 C 1/02, C 09 B 23/00

(30) Priority: **29.11.78 GB 4645978**
29.11.78 US 964479
29.11.78 US 964480

(43) Date of publication of application:
11.06.80 Bulletin 80/12

(84) Designated Contracting States:
BE FR IT

(71) Applicant: **MINNESOTA MINING AND MANUFACTURING COMPANY**
3M Center
Saint Paul, Minnesota 55101(US)

(72) Inventor: **Lea, Bernard Alan**
Minnesota 3M Research Limited
Pinnacles Harlow, Essex(GB)

(72) Inventor: **Burrows, Ronald William**
Minnesota 3M Research Limited
Pinnacles Harlow, Essex(GB)

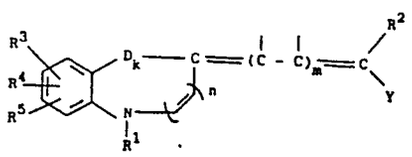
(72) Inventor: **Reece, Jack E.**
3M Center
Saint Paul, Minnesota 55101(US)

(72) Inventor: **Brown, Harvey A.**
3M Center
Saint Paul, Minnesota 55101(US)

(74) Representative: **Baldock, Hugh Charles et al,**
Lloyd Wise, Tregear & Co. Norman House 105-109
Strand
London, WC2R 0AE(GB)

(54) **Dry silver photo-sensitive compositions, dyes for use therein and preparation of such dyes.**

(57) Dry silver photo-sensitive compositions comprising an intimate mixture of a substantially light-insensitive silver compound which upon reduction gives a visible change and sufficient of a silver halide to catalyse said reduction to give a visible change in those areas where the silver halide has been exposed to light and when the mixture is heated in the presence of a reducing agent, and as an acutance dye a compound of the general formula:



(I)

EP 0 012 020 A1

This invention relates to compounds suitable for use as acutance dyes in photosensitive compositions, to the preparation of such compounds and to photosensitive compositions containing the compounds. The invention is particularly concerned with photosensitive compositions of the type known as "dry silver" compositions.

Dry silver photosensitive compositions comprise an intimate mixture of a light sensitive silver halide and another silver compound such as a silver salt of an organic acid, e.g. silver behanate or silver saccharine, which upon reduction gives a visible change and which is substantially light-insensitive. Such a mixture is usually prepared in suspension and the resulting dispersion spread as a layer on a suitable substrate. When dry, the layer is exposed to a light image and thereafter a reproduction of the image can be developed by heating the layer in the presence of a reducing agent such as hydroquinone or certain substituted phenols.

It is because the exposure and development of the layer occur without using water, that these materials are often referred to as dry silver light-sensitive materials. Such materials in which minor amounts of a photosensitive silver halide catalyst-progenitor are associated in catalytic proximity with major amounts of

a heat sensitive oxidation-reduction image forming reaction mixture which reacts more rapidly in the presence of the catalyst resulting upon exposure of the silver halide are well known in the art. Examples of such materials are described in our British Patent No. 1 110 046 and in United States Patent Specification Nos. 3 839 049 and 3 457 075.

We believe, that when the mixture is exposed to light, a latent image is formed in the silver halide. Thereafter, the silver compound can be reduced by heating with the reducing agent, this reduction being catalysed image-wise by the light exposed silver halide. By a suitable choice of temperature, the reduction of the silver compound can be catalysed in the light exposed areas to give a visible darkening while any slight reduction which occurs in the non-light exposed areas is insufficient to give a marked change. Of course, because the silver halide acts as a catalyst progenitor, only very small amounts of it can suffice, e.g. 0.1 to 10% by weight of the mixture. However, large amounts, e.g. up to 15 or even 20% may be desirable in some circumstances.

In order to improve the sharpness or definition of photographic images a dye known as an acutance dye is often incorporated into photo-sensitive compositions.

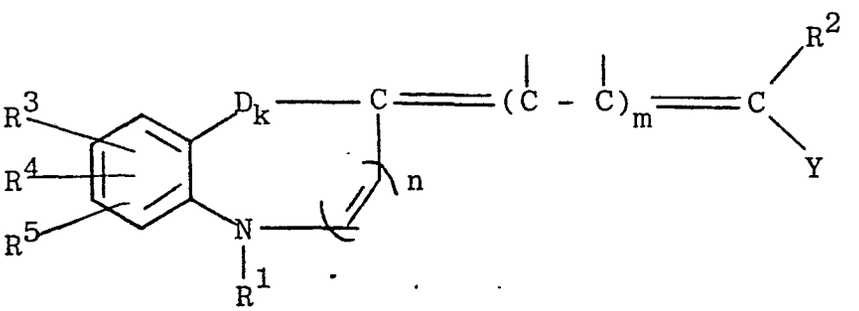
To be effective the acutance dye will absorb at the wavelengths at which the photosensitive composition is sensitive. The longer the path length of the light in the layer of light sensitive composition the greater the attenuation. Therefore, scattered light is attenuated or absorbed to a larger extent that light which impinges directly on a light-sensitive crystal. As a result therefore, although the overall speed of the composition is reduced slightly, scattered light and other light rays which are liable to produce a blurred image are preferentially absorbed and so the overall definition and sharpness of images produced in the layer are increased.

An acutance dye for use in a dry silver composition is preferably heat labile, that is to say, it is destroyed by the heat development of the dry silver composition to one or more compounds which are substantially colour-less.

It is therefore an object of this invention to provide dry silver compositions containing acutance dyes, which absorb light at at least some of those wavelengths to which the composition is sensitive and which are rendered colourless upon heat development of the dry silver composition.

It is also an object of the invention to provide novel compounds suitable for use as acutance dyes in dry silver systems and a method for their preparation.

According to the present invention there is provided a light-sensitive composition comprising an intimate mixture of a substantially light-insensitive silver compound which upon reduction gives a visible change and sufficient of a silver halide to catalyse said reduction to give a visible change in those areas where the silver halide has been exposed to light and when the mixture is heated in the presence of a reducing agent, characterised in that the composition contains as an acutance dye, a compound of the general formula:



(I)

in which R^1 represents an alkyl group containing 1 to 12 carbon atoms,

R^2 represents a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, a phenyl group, a substituted phenyl group of molecular weight less than 350, $-COOR^1$ in which R^1 is as defined above, C_6H_5CO- or $R^6NH.CO$ in which R^6 represents a hydrogen atom or an alkyl, aryl or aralkyl group,

R^3, R^4 and R^5 independently represent a hydrogen atom or a substituent which can be present in a cyanine dye type heterocyclic nucleus,

D represents $-\overset{|}{C}=\overset{|}{C}-$, O, S, Se, $\gtrless C(CH_3)_2$ or $\gtrless NR^7$ in which R^7 represents an alkyl group containing 1 to 4 carbon atoms or CH_3COO-,

Y represents $-CN$ or $-NO_2$,

n is 1 when k is 0 or k is 1 when n is 0, and

m is 0, 1 or 2.

The substituents R^3, R^4 and R^5 independently represent a substituent which, as known in the art, can be present in a cyanine dye type heterocylic nucleus, defined herein as a "cyanine dye compatible substituent", referring to the broadly art accepted knowledge of substituents. A range of such substituents are disclosed for example in United States Patent Specification No. 2 921 067.

Examples of substituents for R^3, R^4 and R^5 include hydrogen or halogen, e.g. chlorine, bromine or iodine, an alkyl group containing 1 to 12 carbon atoms, an alkoxy group containing 1 to 4 carbon atoms, an alkenyl group containing 2 to 4 carbon atoms, $-(CH_2)_pCOOH$ where p is 0, 1, 2 or 3, $-NO_2$, $-NH_2$ or $-NHCOCH_3$, or any two of R^3 to R^5 together represent the carbon atoms needed to complete a fused on benzene ring. Preferably at least one, more preferably at least two, of the substituents R^3 to R^5 represent hydrogen atoms. The most preferred substituents to be represented by each of R^3 to R^5 are hydrogen, chlorine or bromine atoms, or methyl, ethyl, methoxy or ethoxy groups.

It is found that dry silver compositions containing one of the above described compounds as an acutance dye can give excellent sharp images and that the actuance dye will be rendered considerably lighter in colour or

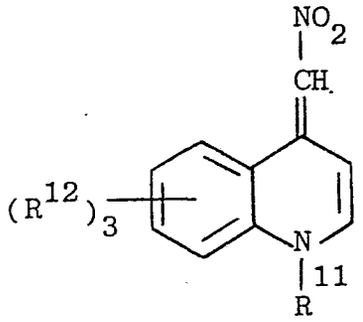
substantially colourless by the heating required to develop the composition. This is surprising in view of the fact that many of these dyes are found not to be decomposed to a colourless state when they are heated on their own to the temperature at which the dry silver compositions are heated for development.

The exact mechanism for this decomposition is not known although the extent of decolourisation has been found to vary when the dry silver systems are altered. Thus a dye may be decomposed to a colourless state when it is present in one particular dry silver system upon development but in a different system the dye may simply be rendered lighter in colour. Thus a compound for use as an acutance dye in a particular dry silver system is selected not only for its efficiency as an acutance dye in that system but also to obtain the desired background after the dry silver composition is developed.

One preferred group of acutance dyes for use in the invention are those in which k=0, n=1, Y is NO_2 and R^2 is $COOC_2H_5$, C_6H_5, C_1 to C_4 alkyl or hydrogen.

A second preferred group of acutance dyes for use in the invention are those in which m=1, k=1, n=0, Y is NO_2, D is oxygen or sulphur and R^2 is $COOR^1$, C_6H_5, substituted phenyl, C_1 to C_4 alkyl or hydrogen.

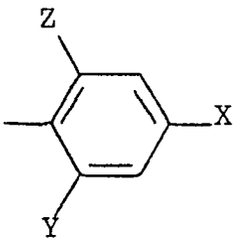
A further group of preferred dyes are 1-alkyl-4-nitromethylene-quinolanes in which the alkyl substituent contains 1 to 4 carbon atoms, particularly those dyes of the general formula:



(II)

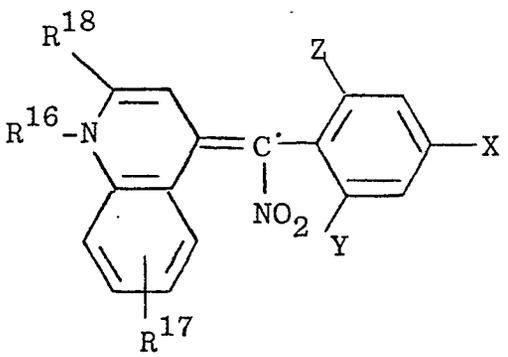
in which R^{11} represents an alkyl group containing 1 to 4 carbon atoms, each R^{12} independently represents a hydrogen or halogen atom, an alkyl or alkoxy group containing 1 to 4 carbon atoms, an alkenyl group containing 2 to 4 carbon atoms, $-(CH_2)_pCOOH$ wherein p is 0, 1, 2 or 3, $-NO_2$, $-NH_2$ or $NHCOCH_3$, or two groups R^{12} together represent the carbon atoms required to complete a fused on benzene ring. Preferably R^{11} represents a methyl or ethyl group, at least one group R^{12} represents a hydrogen atom and each other R^{12} independently represents a hydrogen, chlorine or bromine atom, or a methyl, ethyl, methoxy or ethoxy group.

A further series of dyes are those in which R^2 represents:



in which X, Y and Z independently represent a hydrogen or halogen atom, NO_2, CN or perfluoroalkyl of 1 to 4 carbon atoms, with the proviso that at least one of X and Y is NO_2 and R^3, R^4 and R^5 independently represent a hydrogen or halogen atom, an alkyl or alkoxy of 1 to 4 carbon atoms, alkenyl of 2 to 4 carbon atoms, $-(CH_2)_pCOOH$ wherein p is 0, 1, 2 or 3, $-NO_2$, $-NH_2$ or $-NHCOCH_3$, or any two of the adjacent groups are the atoms necessary to form a fused on benzene ring.

Preferred dyes within the group have the general formula:



(III)

in which R^{16} represents an alkyl group of 1 to 8 carbon atoms,

R^{17} represents alkyl, alkoxy, halogen, NO_2 or aryl, and

R^{18} represents hydrogen, alkyl of 1 to 8 carbon atoms or alkoxy of 1 to 8 carbon atoms.

The acutance dyes can be incorporated into the dry silver compositions of the invention in an amount from 5×10^{-4} to 0.1 mole of acutance dye per kilogram of total dry solids in the composition. Preferably, however the dyes are incorporated in an amount of from 2×10^{-3} to 3×10^{-2} mole of acutance dye per kilogram of dry solids in the composition.

The light-sensitive compositions of the invention will normally be spread for use on a support, suitable supports including, for example, paper, polyester or polyamide film bases, and glass. The composition will normally be prepared as a solution or suspension which is spread as a layer on the support and then the solvent or vehicle is evaporated off to leave a dry photo-sensitive layer. If desired, a coating aid or binder such as polyvinyl butyral, polymethyl methacrylate, cellulose acetate, polyvinyl acetate, cellulose acetate-propionate and cellulose acetate butyrate, can be incorporated in the light-sensitive mixture.

The substantially light-insensitive silver compound is suitably a silver salt of an organic acid. The organic acid can be a C_{12} to C_{29} aliphatic acid and is preferably a C_{16} to C_{25} aliphatic acid. Examples include silver behenate, silver caprate, silver

laurate, silver myristate, silver palmitate, silver stearate, silver arachidate and silver saccharine.

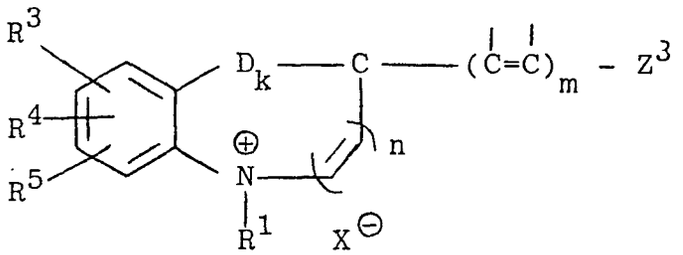
The reducing agent for this substantially light-insensitive silver compound can normally be quite mild. Suitable examples include hydroquinone and substituted phenols such as 1-methyl-4-hydroxy-naphthalene, methyl gallate, catechol, phenylene diamine, p-amino-phenol and 1-phenyl-3-pyrazolidone. The reducing agent can be incorporated into the light-sensitive composition. Alternatively, the composition can be placed in contact with the reducing agent after exposure to light. For example, a light-sensitive coating can be exposed to a light image, placed in contact with a layer containing the reducing agent and the image then developed by heating. Preferably, however, the reducing agent is incorporated in the light-sensitive composition before this is spread on the support. Then the storage stability of the composition can be improved by incorporating in the composition a small amount of a stabilizer such as an acid stabilizer, e.g. succinic acid, benzoic acid or salicylic acid.

The silver halide can be present in amounts of up to 20% by weight of the mixture of silver compounds or can be present in small amounts, e.g. 0.1

to 10% by weight of the mixture of silver compounds. It can be added as such to the substantially light-insensitive compound or formed in situ by adding a soluble halide, e.g. a mercury or sodium halide, to the substantially light-insensitive silver compound. The silver halide can, for example, be chloride, bromide or a mixture of them and/or other silver halides.

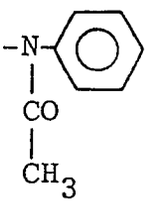
The light-sensitive compositions of the invention can include one or more sensitising dyes to improve their sensitivity to parts of the spectrum other than the shorter wavelengths. Thus dye sensitized dry silver compositions of the present invention can contain an additional acutance dye such as one of those described in our copending British Patent Application No. 1 6677/77.

The compounds of general formula (I) may be prepared by a process which comprises reacting a compound of the general formula:

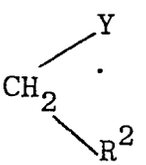


wherein $X^{\ominus}$ represents an anion,

Z^3 is selected from the group consisting of SR^1, wherein R^1 is as defined above, and



with a compound of the formula:



wherein Y and R^2 are as defined above,

the reaction being conducted in the presence of a polar solvent, a base catalyst and an acid binding agent.

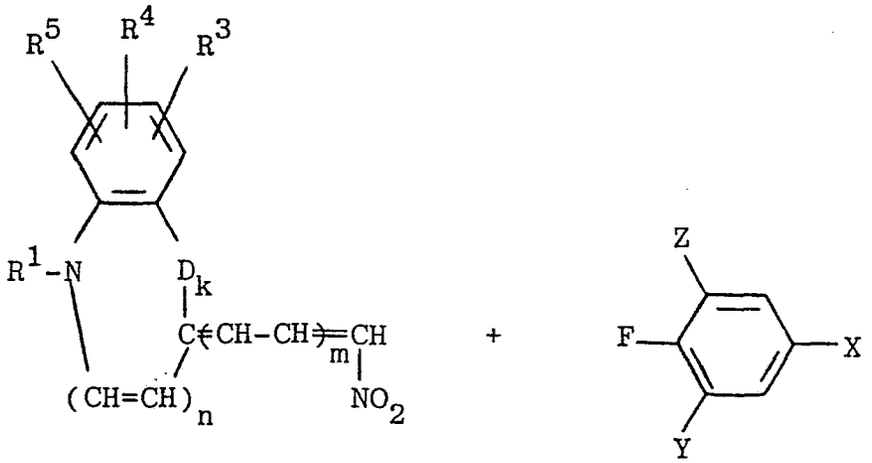
Suitable reagents are well known and fully exemplified in the cyanine/merocyanine dye literature.

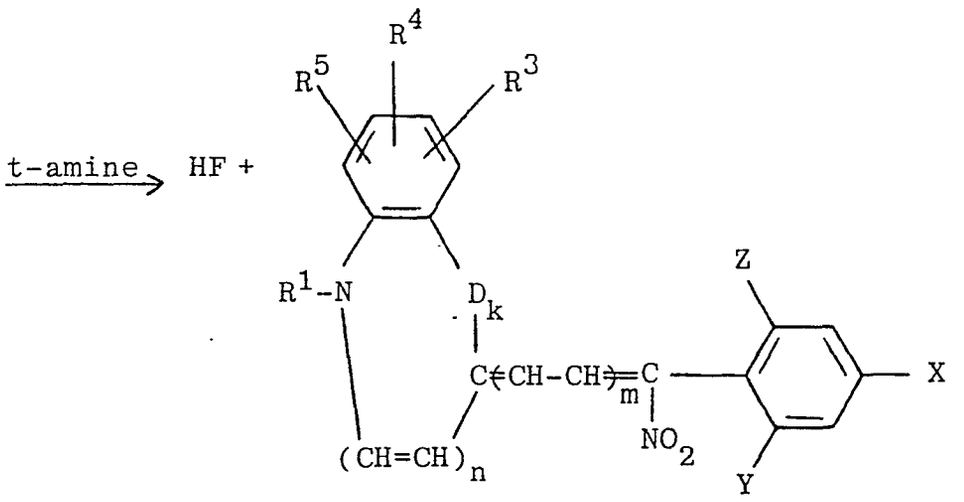
The reaction is preferably carried out in the presence of C_2H_5OH as a solvent and $(C_2H_5)_3N$ as both

catalyst and acid binder. The preparation is analogous to known processes used in the synthesis of merocyanine dyes.

The acutance dyes of general formula (II) can be prepared by processes which are well known. Thus, they can be prepared in a manner analogous to the synthesis of simple merocyanine dyes as described, for example, in British Patent No. 426 718, by reacting nitromethane with a 1-alkyl-4-alkylthio-quinolinium salt in a solvent in the presence of a basic catalyst. They are, however, preferably prepared from 1-alkyl-quinolinium salts by the method described by Leonard, DeWalt and Leubuer in J.A.C.S., 73, 3328, in which a quinolinium quaternary salt is heated with nitromethane in the presence of a base, an oxidising agent and a solvent.

The dyes of general formula (III) may also be made according to the following reaction scheme A:



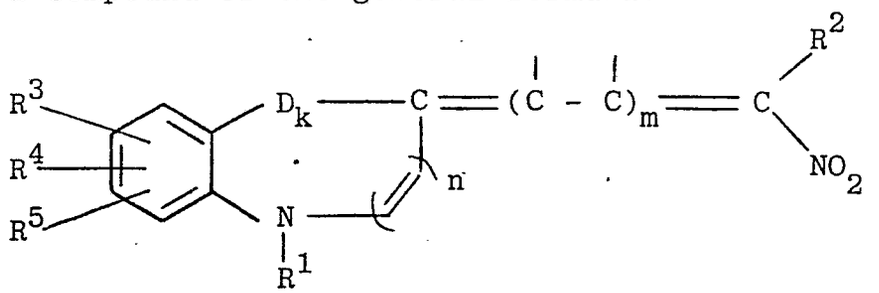


(A)

This method is performed in the presence of a strong tertiary amine such as diisopropylethylamine. For example, in forming 1,4-dihydro-4-(2,4-dinitrophenyl)-nitromethylene-1-methylquinoline (which may also be named 1,4-dihydro-1-methyl-4-(α,2,4-trinitrobenzylidene)quinoline), one would react 4-nitromethylene-1-methyl-1,4-dihydroquinoline with 2,4-dinitrofluorobenzene in diisopropylethylamine.

Certain of the compounds suitable for use as acutance dyes in the present invention are known. Certain compounds of the above formula in which m=0 are disclosed in J.A.C.S. 74,2110, C.A. 55 27373g and United States Patent Specification No. 2 411 507 and other compounds in which m=1 are described by Severin & Bohme in Chem Ber. 101 2925. There is no indication in any of the prior art that such compounds would be suitable for use as acutance dyes in silver halide photothermographic emulsions.

Many of the compounds for use as acutance dyes in accordance with the invention are novel and therefore according to one embodiment of the invention there is provided a compound of the general formula:



wherein:

R^1 represents an alkyl group containing 1 to 12 carbon atoms,

R^3, R^4 and R^5 are cyanine dye compatible substituents,

D represents a member of the group consisting of $-\overset{|}{C}=\overset{|}{C}-$, O, S, Se, $\rangle C(CH_3)_2$ or $\rangle NR^7$ in which R^7 is selected from an alkyl group containing 1 to 4 carbon

atoms or CH_3COO-,

n is 1 when k is 0 or k is 1 when n is 0,

m is 0, 1 or 2,

when m is 0 or 2:

R^2 represents a member selected from the group consisting of an alkyl group, a phenyl group, a substituted phenyl group of molecular weight less than 350, $-COOR^1$ wherein R^1 is as defined above, C_6H_5CO- or $R^6NH.CO-$ wherein R^6 is a member of the group consisting of a hydrogen atom or an alkyl, aryl or aralkyl group,

and when m is 1:

R^2 represents $R^6NH.CO$ wherein R^6 is as defined above.

The invention will now be illustrated by the following Examples.

Example 1

Preparation of 4-(cyano-4'-nitrophenylmethylene)-1-methyl-quinolane (Compound No. 14)

1-Methyl-4-methylthio-quinolinium toluene-4-sulphonate (1.83 g) was placed in ethanol (20 ml) and 4-nitrophenylacetonitrile (0.81 g) added. The mixture was warmed, triethylamine (0.8 ml) added and the resulting mixture heated under reflux for 15 minutes. The dye which separated from the hot solution was filtered off and the crude compound (1.2 g) was twice crystalised from toluene (200 ml) to give magenta needles (0.9 g) having a melting point of 203 to 204°C. In methanolic solution the dye exhibited $\varepsilon = 2.0 \times 10^4$ at λmax 495 nm.

Example 2

Preparation of 4-(ethoxycarbonyl-nitromethylene)-1-methyl-quinolane (Compound No. 12)

1-Methyl-4-methylthio-quinolinium toluene-4-sulphonate (1.8 g) and ethyl nitroacetate (1 ml) were placed in ethanol (10 ml) and the mixture warmed. After the addition of triethylamine (0.7 ml) the whole was heated under reflux for 10 minutes. The product crystallised upon cooling and was filtered off. The crude product was purified by boiling with ethanol (70 ml), to give both an undissolved residue (0.8 g) and a crystallised sample (0.25 g) Both samples formed yellow plates with

melting point of 203 to 206°C and the recrystallised sample showed $\varepsilon = 6 \times 10^3$ in methanolic solution at λ max 465 nm.

Analysis:

Calculated:	N 10.0%	
Found:	N 10.2%	

Example 3

Preparation of 3-ethyl-2(3-nitro-3-phenyl-allylidene)-2,3-dihydrobenzothiazole (Compound No. 21)

2-Acetanilino-3-ethyl-benzothiazolium iodide (4.5 g) was placed in ethanol (25 ml) and phenyl nitromethane (1.4 g) added. The mixture was warmed, triethylamine (1.4 ml) added and the resulting mixture heated under reflux for 20 minutes. Upon cooling, a mixture of product and trimethincyanine dye was deposited. This was filtered off and the product extracted with toluene. The extracted solid was then crystallised from ethanol (350 ml) to give dark green coloured plates (2.4 g) having a melting point of 155°C. In methanolic solution the dye exhibited $\varepsilon = 6.2 \times 10^4$ at λ max 523 nm.

Analysis:

Calculated:	N 8.64%;	S 9.87%
Found:	N 8.69%;	S 9.85%

Example 4

Preparation of 3-ethyl-2-(3-ethoxycarbonyl-3-nitro-allylidene)-2,3-dihydrobenzoxazole (Compound No. 20)

2-Acetanilino-3-ethyl-benzoxazolium iodide (2.17 g) was placed in ethanol (10 ml) and ethyl nitroacetate (1.0 ml) added. The mixture was warmed, triethylamine (0.7 ml) added and the resulting mixture heated under reflux for 7 minutes. The dye separated upon cooling and after filtration the crude product (1.2 g) was crystallised from toluene (17 ml) to give yellow needles (1.05 g) having a melting point of 172 to 175°C. In methanolic solution the dye exhibited $\varepsilon = 5.6 \times 10^4$ at λ max 452 nm.

Analysis:

Calculated:	C 59.21%;	H 5.26%;	N 9.21%
Found:	C 58.90%;	H 5.59%;	N 9.10%

Example 5

Preparation of 3-ethyl-2-(5-ethoxycarbonyl-5-nitro-penta 2,4-dienylidene)-2,3-dihydrobenzothiazole (Compound No. 34)

2-(4'-Acetanilino-1,3-butadienyl)-3-ethyl benzothiazolium iodide (4.76 g), ethyl nitroacetate (1.2 ml), ethanol (100 ml) and triethylamine were mixed and stirred at room temperature for 15 hours. The whole was then evaporated and the residue extracted with six portions

(50 ml) each of toluene at 50°C. The residue obtained by evaporation of the toluene was crystallised from aqueous methanol to give dark microcrystals (0.5 g) with a melting point of 125°C. In methanolic solution the compound showed $\varepsilon = 4.6 \times 10^4$ at λ max 574 nm.

Analysis:

Calculated:	C 59.0%;	H 5.20%;	N 8.1%
Found:	C 59.5%;	H 5.4%;	N 8.1%

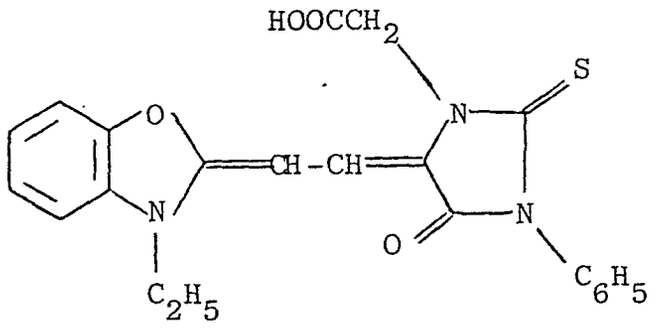
Example 6

Evaluation of acutance dyes

A dry silver composition was first prepared. Under room light a 1000 g dispersion containing 12.5 parts of silver behenate in 87.5 parts of solvent which in turn comprised 75 parts butan-2-one and 25 parts toluene was charged to a mixing vessel maintained at 15°C. 20 g of polyvinyl butyral resin (Butvar, B-76) and 10 g of 1-methyl-2-pyrrolidinone were added and the mixture stirred for 30 minutes.

Under Wratten 1A safelight a mixture containing hydrobromic acid (15 ml, 2.0 molar in ethanol), hydroiodic acid (7 ml, 0.1 molar in ethanol), and mercuric bromide (4 ml, 0.5 molar in ethanol) was added with stirring. After 20 minutes an additional 40 g of Butvar B-76 was added, followed after five minutes by 10 g 2,6-bis-(2'-hydroxy-3'-tertiary-butyl-5'-methyl-benzyl)-4-methyl-

phenol available from American Cyanamide under the name A080 and 6 g phthalazinone. After 20 minutes 12 g of a solution containing 2 mg of the following dye:



per gram of 1-methyl-2-pyrrolidinone was added and the mixture stirred for an additional 30 minutes.

Equimolar amounts of the acutance dyes to be tested were added to appropriate containers and dispersed in 2 ml of butane-2-one. 40 g portions of the light sensitive dispersion prepared above were added to each, the mixture shaken, left to stand 30 minutes, then shaken again prior to coating.

Knife coatings 100 microns thick on polyester sheets were prepared from each sample and dried 3.5 to 4.0 minutes at 90°C. These dried coatings were overcoated with a solution containing 97 parts butan-2-one and 3 parts vinyl chloride vinyl acetate copolymer available from Union Carbide under the name VYNS with the knife set 50 microns above the base and dried as before.

The performance of these compositions was then evaluated.

A combination of a tungsten source, a narrow band filter at a wavelength closely matching the spectral absorbance of each dye and an aperture target overlaid with a 0 to 4 continuous density wedge in a vacuum frame, was used to make contact exposures at a wavelength closely matching the spectral absorbance maximum of each dye. The strips were then processed by heating for 20 seconds in a fluorochemical bath and examined for flare of the image.

The acutance property of the dyes was classified very good, good, fair by examining the sharpness of the image with the naked eye.

The background before and after processing was observed.

The following Table 1 reports compounds of the general formula (I).

The mode of preparation of the compounds is indicated in the final column, in which:

1. refers to a preparation disclosed in Chem.Ber. 101 2295,
2. refers to a preparation analogous to Example 2,
3. refers to a preparation analogous to Example 3,
4. refers to a preparation analogous to Example 5.

Table 1

Cmpd. No.	R^1	R^2	R^3, R^4, R^5 (R^3 in the 6-position)	m	k,n	D	Y	λ max (MeOH) nm	M.P. °C	Acutance	Background		Prep.
											before processing	after processing	
1	CH_3	$COOC_2H_5$	H, H, H	0	1,0	-CH=CH-	CN	410	183-4	good	p.yellow	lighter	2
2	C_2H_5	$COOC_2H_5$	CH_3O, H, H	0	1,0	-CH=CH-	CN	435	123-5	good	p.yellow	lighter	2
3	CH_3	$COOC_2H_5$	H, H, H	0	0,1	—	CN	433	183	v. good	p.yellow	lighter	2
4	CH_3	C_6H_5	H, H, H	0	0,1	—	NO_2	510		fair	red	v. pale	2
5	CH_3	C_6H_5	H, H, H	0	1,0	S	NO_2	409	188	good	p.yellow	lighter	2
6	CH_3	C_6H_5	H, H, H	0	1,0	-CH=CH-	NO_2	490	215-7 d	fair	pink	lighter	2
7	CH_3	$-C_6H_4NO_2$	H, H, H	0	1,0	S	NO_2	406	265 d	v. good	p.yellow	lighter	2
8	CH_3	$-C_6H_4NO_2$	H, H, H	0	1,0	-CH=CH-	NO_2	404(480)	217	v. good	pink	lighter	2
9	CH_3	C_6H_5CO-	H, H, H	0	1,0	S	NO_2	392	220	good	yellow	lighter	2
10	CH_3	C_6H_5CO-	H, H, H	0	0,1	—	NO_2	466	170	good	yellow	v. pale	2
11	CH_3	$-C_6H_4NO_2$	H, H, H	0	0,1	—	NO_2	410(500)	212-3d				2
12	CH_3	$COOC_2H_5$	H, H, H	0	0,1	—	NO_2	465	d 203-6				Ex.2
13	CH_3	C_6H_5NHCO	CH_3, H, H	0	0,1	—	NO_2	467					2
14	CH_3	$C_6H_4NO_2$	H, H, H	0	0,1	—	CN	495					Ex.1

Table 1 Contd.

Cmpd. No.	R^1	R^2	R^3, R^4, R^5	m	k,n	D	Y	λ max (MeOH) nm	M.P. °C	Acutance	Background		Prep.
											before processing	after processing	
15	C_2H_5	$C_6H_4NO_2$	H, H, H	1	1,0	S	CN	520	260-1 d	good	magenta	pale	3
16	C_2H_5	$C_6H_4NO_2$	H, H, H	1	1,0	O	CN	488	228-30d	good	red	pale	3
17	C_2H_5	$C_6H_4NO_2$	H, H, H	1	1,0	-CH=CH-	CN	540 (570)	275 d	good	violet	pale	3
18	C_2H_5	$C_6H_5NO_2$	H, H, H	1	0,1	—	CN	620 (583)	245 d	good	blue	v. pale	3
19	C_2H_5	$COOC_2H_5$	H, H, H	1	1,0	S	NO_2	483	178-180	good	orange	pale	3
20	C_2H_5	$COOC_2H_5$	H, H, H	1	1,0	O	NO_2	452	172-5	good	yellow	pale	Ex.4
21	C_2H_5	C_6H_5	H, H, H	1	1,0	S	NO_2	523	155	good	magenta	colour-less	Ex.3
22	C_2H_5	C_6H_5	H, H, H	1	1,0	O	NO_2	487	188	good	orange	colour-less	3
23	C_2H_5	C_6H_5	H, H, H	1	1,0	-CH=CH-	NO_2	554	135-140	good	magenta	pale	3
24	C_2H_5	C_6H_5	H, H, H	1	0,1	—	NO_2	602	157	v. good	blue	colour-less	1
25	CH_3	C_6H_5	H, H, H	1	0,1	—	NO_2	602	195	v. good	blue	colour-less	1

Table 1 Contd.

Cmpd. No.	R^1	R^2	R^3, R^4, R^5	m	k,n	D	Y	λ max (MeOH) nm	M.P. °C	Acutance	Background		Prep.
											before processing	after processing	
26	C_2H_5	C_2H_5	H, H, H	1	0,1	—	NO_2	604	140	v. good	blue	colourless	1
27	CH_3	C_2H_5	H, H, H	1	0,1	—	NO_2	603	208	v. good	blue	colourless	1
28	C_2H_5	CH_3	H, H, H	1	0,1	—	NO_2	603	146	v. good	blue	colourless	1
29	CH_3	CH_3	H, H, H	1	0,1	—	NO_2	604	228	v. good	blue	colourless	1
30	C_2H_5	C_6H_5CONH	H, H, H	1	1,0	S	NO_2	496	238				3
31	C_2H_5	C_6H_5CONH	H, H, H	1	1,0	O	NO_2	462	233				3
32	C_2H_5	C_6H_5CONH	H, H, H	1	1,0	-CH=CH-	NO_2	504	220 d				3
33	C_2H_5	C_6H_5CONH	H, H, H	1	0,1	—	NO_2	534					3
34	C_2H_5	$COOC_2H_5$	H, H, H	2	1,0	S	NO_2	574	125	fair	blue	lighter	Ex.5
35	C_2H_5	C_6H_5CO-	H, H, H	2	1,0	S	NO_2	590	203				4

Example 7

A series of dyes of general formula (II) were prepared according to the method described in J.A.C.S. 73, 3328.

The dyes prepared are those having the values of R^{11} and one of the substituents R^{12}, the remaining substituents R^{12} representing hydrogen atoms, as set out in the following Table 2.

Table 2

Compound No.	R^{11}	R^{12}	Melting point °C	λ max nm
36	CH_3-	H-	204 (d)	466
37	CH_3-	6-CH_3O-	213-215 (d)	473
38	CH_3-	6-CH_3-	208-210 (d)	470
39	C_2H_5-	H-	157-159	469
40	CH_3-	6-Cl-	238 (d)	476
41	C_2H_5-	6-Cl-	171 (d)	475
42	CH_3-	8-CH_3O-	208 (d)	463
43	C_2H_5-	8-CH_3O-	173-175 (d)	467

(d) = with decomposition after melting.

Compounds 36 to 43 were evaluated for use as acutance dyes in a similar manner to those in Example 6. Table 3 summarises the amount of each dye used in the dry silver compositions.

Table 3

Composition	Compound No.	Molecular weight	Mg of dye in 2 ml butan-2-one
A	(Control) None	-	-
B	36	202	7.2
C	37	232	8.3
D	38	216	7.7
E	39	216	7.7
F	40	260	9.3
G	41	250	8.9
H	42	232	8.3
J	43	246	8.8

The acutance properties were measured as in Example 6 with the exception that microdensitometer traces across the width of the image at D = 2.0 (obtained after processing the exposed strips 20 seconds at 127^{o}C in a fluorocarbon oil bath to give reproducible heating for these tests) were used to judge the effectiveness of each dye.

The widths reported are the measured widths in centimetres of the density profile of each image as obtained from the microdensitometer chart. All measurements were carried out at D = 1.5.

The results of testing the compositions are given in Table 4.

Table 4

Coating of Composition	Microdensitometer traces		Flare	Background	
	Target width cm	Image width cm		Before Processing	After Processing
A	2.95	22.85	6.75	pale pink	colourless
B	2.90	8.76	2.02	yellow	colourless
C	2.95	7.60	1.58	orange-yellow	colourless
D	2.80	6.60	1.36	yellow	colourless
E	2.95	6.90	1.34	yellow	colourless
F	2.90	11.50	2.97	orange-pink	colourless
G	2.90	7.10	1.45	orange-yellow	colourless
H	2.75	13.30	3.84	pink	colourless
J	2.90	9.40	2.24	yellow	very pale yellow

$$\text{Flare} = \frac{\text{Image width - target width}}{\text{target width}}$$ for perfect results, flare = 0

All exposures made at 480 nm.

As can be seen from these results the presence of a yellow acutance dye in a dry silver composition according to the invention significantly reduces flare as compared with the dry silver composition A not containing any acutance dye.

Example 8

The following compounds of general formula (III) reported in Table 5 were prepared in accordance with reaction scheme (A).

Table 5

Compound No.	R^{16}	R^{17}	R^{18}	X	Y	Melting point (°C) (decomposition temperature)
44	C_2H_5	H	H	NO_2	NO_2	228-230
45	C_3H_7	H	H	NO_2	NO_2	215
46	C_2H_5	H	H	CN	NO_2	232-234
47	CH_3	H	CH_3	NO_2	NO_2	237-239
48	C_2H_5	H	H	NO_2(Z)	NO_2	230
49	CH_3	OCH_3(4)	H	NO_2	NO_2	205-206
50	CH_3	OCH_3(4)	H	CN	NO_2	229-231

In Table 5 the numbers in parentheses indicate the position of attachment for particular substituents. Infrared analysis and nucleus magnetic resonance analysis confirmed the structure of each of these dyes.

Example 9

Four hundred grams of a dispersion containing 13 parts by weight of silver behenate in 87 parts of a solvent composed of 67 parts by weight methylethylketone, 26 parts by weight toluene, and 7 parts by weight methylisobutylketone was charged to a temperature-controlled stirred reaction vessel at 15°C. Dark room conditions were maintained during all subsequent work.

The following materials were added sequentially with 20 to 30 minutes of stirring between separate additions.

A. 2 g of 1-methyl-2-pyrrolidinone in 6 g of polyvinylbutyral,

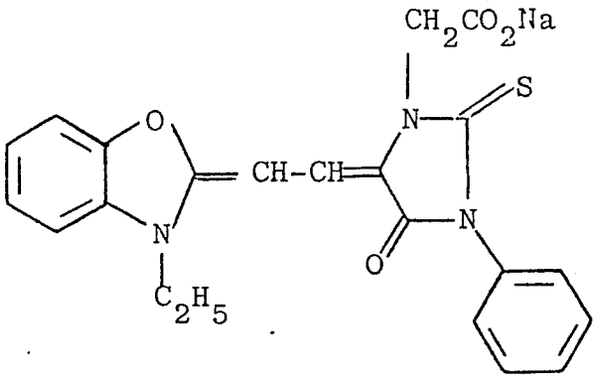
B. 8 ml of 2M HBr (in ethanol) and 3.2 ml of 0.1M HI (in ethanol),

C. 10 g of a copolymer derived from 91% by weight vinylchloride, 3% vinylacetate, and 6% by weight vinyl alcohol polymerized to a molecular weight of about 23,000, and 24 g of polyvinyl butyral,

D. 1.8 ml of 0.5M $HgBr_2$ (in ethanol) was added with 5 minutes of stirring,

E. 5.2 g of phthalazinone and 7.8 g of 2,6-bis-(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol,

F. 2.8 ml of a sensitizer solution having 5 mg/ml of the sensitizer in N-methylpyrrolidone, the sensitizer having the formula:

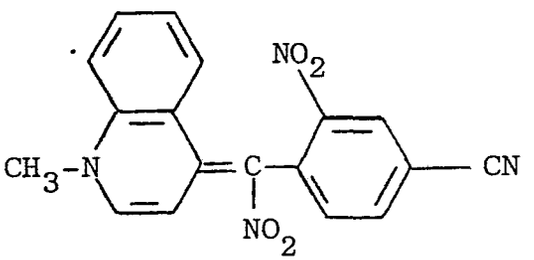


10 mg of each candidate acutance dye was weighed into separate vessels with 3 ml of methylethylketone to dissolve or disperse the dye. 50 g portions of the light-sensitive dispersion formed above were combined with the dye solutions and to portions of methylethylketone alone as a control. All materials were stirred for three minutes. The portions were then allowed to stand at room temperature for 30 minutes, then they were knife coated at 85 microns thickness on polyester and dried for four minutes at 85°C. Each sample was topcoated with a 50 micron knife coating of a vinylchloride/vinylacetate copolymer as a 5% by weight solution in methylethylketone.

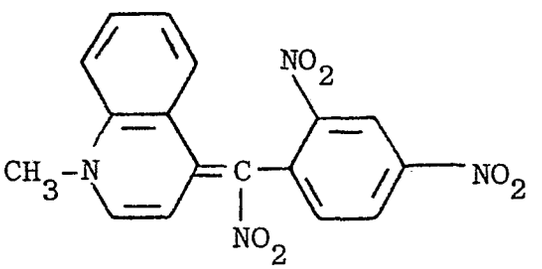
The produced film samples were exposed at the wavelengths indicated below through a 0.25 mm aperture mask overlaid with a continuous density wedge in a vaccum frame. This permitted an easy comparison of image flare at equivalent optical densities after development

for 15 seconds at 127°C in an inert fluorocarbon chemical bath. All dye samples had markedly less flare than the control samples, particularly at an optical density of 2.0. Except for the Compound No. 51, no samples left significant visible stain after processing. The dye of Compound No. 51 left a magenta stain which faded within an hour under room light. The dyes used in the tests were as follows:

Compound No. 51 (560 nm),



Compound No. 52 (500 nm),



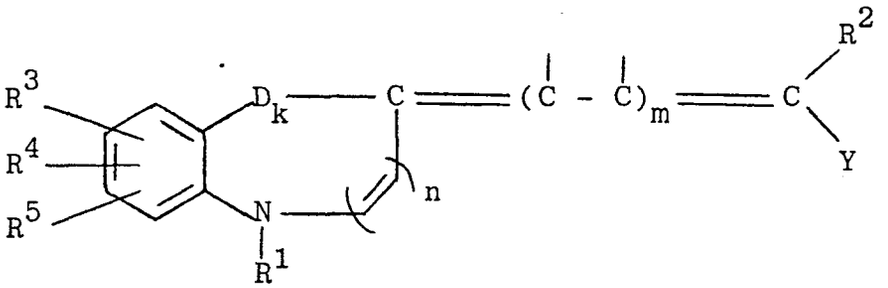
Compound No. 44 (500 nm),

Compound No. 45 (500 nm),

Compound No. 48 (500 nm).

CLAIMS:

1. A light-sensitive composition comprising an intimate mixture of a substantially light-insensitive silver compound which upon reduction gives a visible change and sufficient of a silver halide to catalyse said reduction to give a visible change in those areas where the silver halide has been exposed to light and when the mixture is heated in the presence of a reducing agent, characterised in that the composition contains as an acutance dye, a compound of the general formula:



(I)

in which R^1 represents an alkyl group containing 1 to 12 carbon atoms,

R^2 represents a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, a phenyl group, a substituted phenyl group of molecular weight less than 350, $-COOR^1$ in which R^1 is as defined above, C_6H_5CO- or $R^6NH.CO$ in which R^6 represents a hydrogen atom or an alkyl, aryl or aralkyl group,

R^3, R^4 and R^5 independently represent a hydrogen atom or a substituent which can be present in a cyanine dye type heterocyclic nucleus,

D represents $-\overset{|}{C}=\overset{|}{C}-$, O, S, Se, $>C(CH_3)_2$ or $>NR^7$ in which R^7 represents an alkyl group containing 1 to 4 carbon atoms or CH_3COO-,

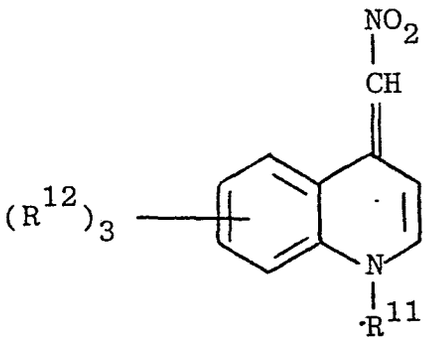
Y represents -CN or $-NO_2$,

n is 1 when k is 0 or k is 1 when n is 0, and

m is 0, 1 or 2.

2. A composition as claimed in Claim 1 in which the acutance dye is a 1-alkyl-4-nitromethylene-quinolane, the alkyl substituent containing 1 to 4 carbon atoms.

3. A composition as claimed in Claim 2 in which the acutance dye has the general formula:

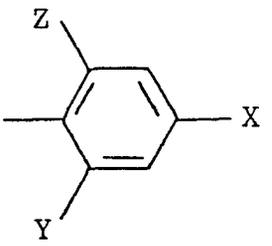


in which R^{11} represents an alkyl group containing 1 to 4 carbon atoms, each R^{12} independently represents a hydrogen or halogen atom, an alkyl or alkoxy group containing 1 to 4 carbon atoms, an alkenyl group containing 2 to 4 carbon atoms, $-(CH_2)_pCOOH$ where p is 0, 1, 2 or 3, $-NO_2$, $-NH_2$ or $NHCOCH_3$, or two groups R^{12} together represent the carbon atoms required to complete a fused on benzene ring.

4. A light-sensitive composition as claimed in Claim 3

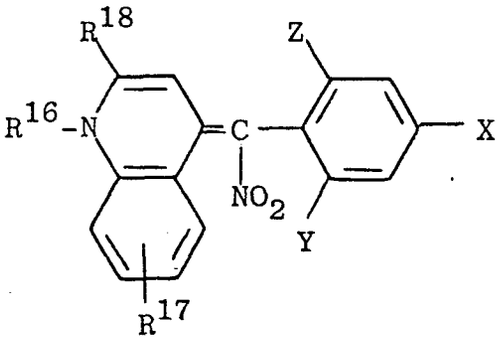
in which R^{11} represents a methyl or ethyl group, at least one group R^{12} represents a hydrogen atom and each other R^{12} independently represents a hydrogen, chlorine or bromine atom, or a methyl, ethyl, methoxy or ethoxy group.

5. A composition as claimed in Claim 1 in which R^2 represents:



in which X, Y and Z independently represent a hydrogen or halogen atom, NO_2, CN or perfluoroalkyl of 1 to 4 carbon atoms, with the proviso that at least one of X and Y is NO_2 and R^3, R^4 and R^5 independently represent a hydrogen or halogen atom, an alkyl or alkoxy of 1 to 4 carbon atoms, alkenyl of 2 to 4 carbon atoms, $-(CH_2)_pCOOH$ wherein p is 0, 1, 2 or 3, $-NO_2$, NH_2 or $-NHCOCH_3$, or any two of the adjacent groups are the atoms necessary to form a fused on benzene ring.

6. A composition according to Claim 1 having the formula:



in which R^{16} represents an alkyl group of 1 to 8 carbon atoms,

R^{17} represents alkyl, alkoxy, halogen, NO_2 or aryl,

R^{18} represents hydrogen, alkyl of 1 to 8 carbon atoms or alkoxy of 1 to 8 carbon atoms, and

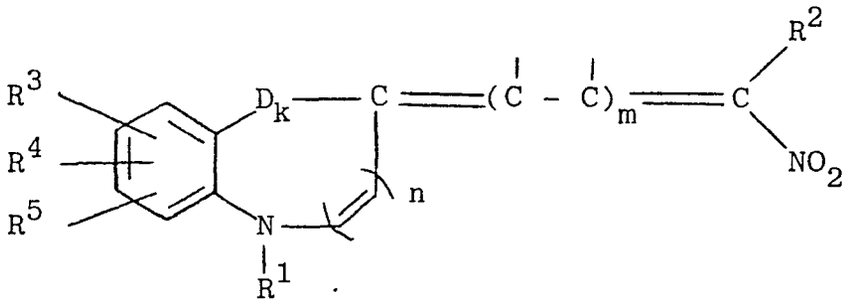
X, Y and Z independently represent hydrogen, NO_2, CN, halogen and perfluoroalkyl of 1 to 4 carbon atoms with the proviso that at least one of X, Y and Z represent NO_2.

7. A light-sensitive composition as claimed in Claim 1 in which k=0, n=1, R^2 represents $COOC_2H_5$, C_6H_5, an alkyl group of 1 to 4 carbon atoms or hydrogen and Y is NO_2.

8. A light-sensitive composition as claimed in Claim 1 in which m=1, k=1, n=0, D is a member of the group consisting of oxygen and sulphur, R^2 is a member of the group consisting of $COOR^1$, C_6H_5, a substituted phenyl group of molecular weight less than 350, an alkyl group of 1 to 4 carbon atoms and hydrogen and Y is NO_2.

9. A light-sensitive composition as claimed in any preceding claim, in which the dye is used in an amount of from 5×10^{-4} to 0.1 mole per kilogram of total dry solids in the composition.

10. A compound of the general formula:



wherein:

R^1 represents an alkyl group containing 1 to 12 carbon atoms,

R^3, R^4 and R^5 are cyanine dye compatible substituents,

D represents a member of the group consisting of $-\overset{|}{C}=\overset{|}{C}-$, O, S, Se, $\diagdown C(CH_3)_2$ or $\diagdown NR^7$ in which R^7 is selected from an alkyl group containing 1 to 4 carbon atoms or CH_3COO-,

n is 1 when k is 0 or k is 1 when n is 0,

m is 0, 1 or 2,

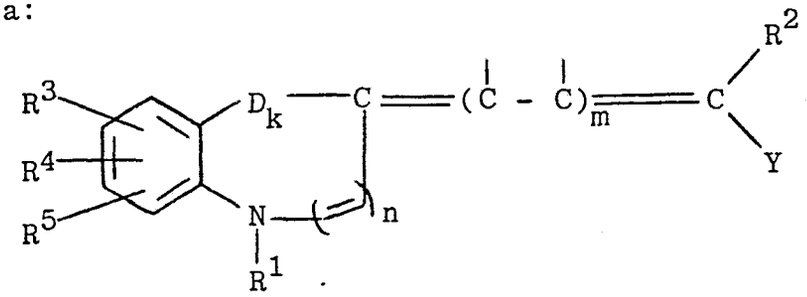
<u>when m is 0 or 2</u>:

R^2 represents a member selected from the group consisting of an alkyl group, a phenyl group, a substituted phenyl group of molecular weight less than 350, $-COOR^1$ wherein R^1 is as defined above, C_6H_5CO- or $R^6NH.CO$ wherein R^6 is a member of the group consisting of a hydrogen atom or an alkyl, aryl or aralkyl group,

<u>and when m is 1</u>

R^2 represents $R^6NH.CO$ wherein R^6 is as defined above.

11. A method of preparing a compound of the general formula:



wherein:

n is 1 when k is 0 or k is 1 when n is 0,

m is 0, 1 or 2,

Y is a member selected from the group consisting of -CN and NO_2,

R^1 represents an alkyl group containing 1 to 12 carbon atoms,

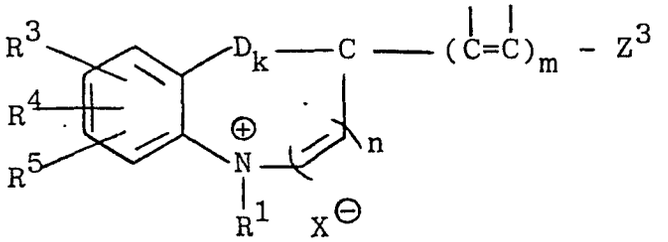
R^2 is a member selected from the group consisting of a phenyl group, a substituted phenyl group of molecular weight less than 350, $-COOR^1$ wherein R^1 is an alkyl group of 1 to 12 carbon atoms, C_6H_5CO- or $R^6NH.CO-$ wherein R^6 is a member of the group consisting of a hydrogen atom, alkyl, aryl or aralkyl group and when m is 1 or 2 R^2 may additionally represent a member of the group consisting of a hydrogen atom and an alkyl group having 1 to 4 carbon atoms,

R^3, R^4 and R^5 are cyanine dye compatible substituents,

D represents a member of the group consisting of $-\overset{|}{C}=\overset{|}{C}-$, O, S, Se, $>C(CH_3)_2$ or $>NR^7$ wherein R^7 is

selected from the group consisting of an alkyl group containing 1 to 4 carbon atoms and CH_3COO-,

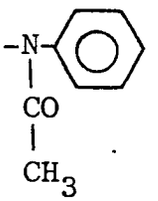
which comprises reacting a compound of the general formula:



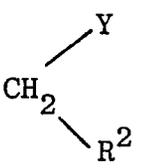
wherein:

$X^{\ominus}$ represents an anion,

Z^3 is selected from the group consisting of SR^1, wherein R^1 is as defined above, and



with a compound of the formula:



wherein Y and R^2 are as defined above,

the reaction being conducted in the presence of a polar solvent, a base catalyst and an acid binding agent.

European Patent Office

EUROPEAN SEARCH REPORT

0012020
Application number
EP 79 30 2730

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 033 948 (H.A. BROWN) * The claims *	1
A	US - A - 3 984 248 (D.M. STURMER) * The claims *	1
A	US - E - Re 29 168 (D.W. HESELTINE et al.) * The claims *	1
X	FR - A - 965 555 (PHOTO PRODUITS GEVAERT) * Abstract; .. the compounds XII and XIII *	11
	GB - A - 849 741 (ILFORD) * The claims *	11
D	CHEMISCHE BERICHTE, vol. 101, 1968, Verlag Chemie Weinstein Bergstrasse DE T. SEVERIN et al.: "Darstellung von Nitromerocyaninen", pages 2925-2930. * Pages 2925-2930 *	10
	FR - A - 2 389 159 (FUJI PHOTO) * The claims; page 11, lines 1-30 *	11

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

G 03 C 1/84
G 03 C 1/02
C 09 B 23/00

TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

G 03 C 1/84
G 03 C 1/02
C 09 B 23/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	25-02-1980	RASSCHAERT

EPO Form 1503.1 06.78