⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 345 444 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **89107013.8**

⑤① Int. Cl.⁴: **G03C 7/02**

㉒ Date of filing: **19.04.89**

㉚ Priority: **10.05.88 IT 2052388**

㊸ Date of publication of application:
13.12.89 Bulletin 89/50

(84) Designated Contracting States:
DE FR GB

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㊹ Light-sensitive non-silver photographic element and process for incorporating hydrophobic compositions into hydrophilic colloid compositions.

㊼ The imaging methods which make use of imaging ionic dye-counterion combinations, dissolved in water-immiscible oil solvents dispersed in hydrophilic media, give better results if dispersion is made in the presence of a sorbitan ester non-ionic surfactant (including a polyoxyethylene derivative thereof) having a HLB (hydrophilic-lipophilic balance) value in the range from 4 to 10 in absence of anionic surfactants.

Light-Sensitive Non-Silver Photographic Element And Process for Incorporating Hydrophobic Compositions into Hydrophilic Colloid Compositions

FIELD OF THE INVENTION

The present invention relates to a light-sensitive non-silver photographic element including a support base and a hydrophilic layer coated thereon said hydrophilic layer including an ionic dye-counter ion imaging combination dissolved in water-immiscible organic solvent droplets dispersed therein in reactive association with a non-ionic surfactant compound.

BACKGROUND OF THE ART

Non-silver imaging methods capable of recording a positive image simply upon exposure to radiation of selected wavelength are known in the art; the radiation absorbed by the dye which is in reactive association with an appropriate counter ion causes the dye to bleach. Non-silver imaging methods are based on the fact that light absorption by a dye sensitizes the dye's own destruction or decolorization. For example, a yellow dye absorbs blue light and the excited dye thus formed reacts with an activator which releases a species to bleach the dye. Similarly, green and red lights would respectively cause the destruction of the magenta and cyan dyes. Thereafter the element may be stabilized to fix the image by destruction of the counter ion or by separation of the dye from the counter ion.

In other non-silver imaging methods, the same ionic dye-counter ion combinations act as photoinitiators for free-radical addition polymerizable compositions.

Such imaging dyes are normally ionic dyes (that is a dye with a positive or negative charge) associated with an appropriate counter ion as described in British Patent Application No. 84 301 156. Particularly, a dye$^-$-iodonium$^+$ combination has been described in EP patent applications Nos. 120,601 and 175,504 and dye$^+$-borate$^-$ combination has been described in US patent No.4,307,182. European Patent Application No. 223,587 describes analogous ionic dye-counter ion combinations in association with free-radical polymerizable compounds and color forming compounds.

The dyes used may be of any color and any chemical class which is capable of bleaching upon exposure to radiation of selected wavelength in the presence of a counter ion.

Generally, many photographic additives, such as the ionic dye-counter ion combinations, are hardly soluble in water and, when soluble in water-miscible organic solvents, they are incompatible with hydrophilic colloid compositions when incorporated therein through said organic solutions.

One way of introducing hydrophobic compounds into hydrophilic colloidal binders is the so-called dispersion technique. Briefly, according to this technique, as described in US patent 2,322,027, the hydrophobic photographic additives are dissolved in water-immiscible high-boiling organic solvents (also called in the art permanent solvents, crystalloidal solvents, oil-type solvents, oil-formers and the like) and the resulting organic solution is added to an aqueous composition containing a hydrophilic colloid (gelatin) and a dispersing agent (normally including an anionic surfactant). The mixture is then passed through a homogenizing apparatus (colloidal mill) to form a dispersion of fine droplets of said organic solvent containing the hydrophobic photographic additives. In some cases it may be advantageous to facilitate the dissolution of the additives by use of an auxiliary water-immiscible low-boiling organic solvent, which is removed afterwards by evaporation, as described e.g. in US patents 2,801,170; 2,801,171 and 2,949,360. The obtained dispersion is then mixed with the hydrophilic colloid composition (gelatin silver halide emulsion or other gelatin-containing composition) which is used to form (by coating) the photographic layer.

Organic solvents for dispersing photographic additives are well known in the art, as disclosed for example in US patents 2,322,027; 2,801,171; 2,835,579; 2,533,514; 3,554,755; 3,748,141; 3,779,765; 4,353,979; 4,430,421 and 4,430,422.

These high-boiling water-immiscible organic solvents as well as methods to obtain a dispersion of hydrophobic compounds in hydrophilic binders have been mainly developed for use in color silver halide photography, wherein the so-called "dispersed couplers" are used to obtain color images upon development of exposed silver halide grains.

US patent 3,860,425 refers to the above mentioned dispersion technique in which the dispersed phase is an oil such as dibutylphthalate, butyllaurate, tricresylphthalate and tricresylphosphate and the material dissolved in such dispersed oil is an oleophilic material such as a dye for silver dye bleaching process, a coupler free of water solubilizing group, an ultraviolet absorber, an antioxidant, a dye image stabilizer, or an optical brightener, the dispersion being stabilized with a non-ionic agent used in combination with an anionic agent.

SUMMARY OF THE INVENTION

In the present invention,the imaging methods which make use of ionic dye-counter ion imaging combinations dissolved in water-immiscible oil solvents dispersed in hydrophilic media can give better results if the dispersion is made in presence of a sorbitan ester non-ionic surfactant (including a polyoxyethylene derivative thereof) having a HLB (hydrophilic-lipophilic balance) value in the range from 4 to 10 in absence of anionic surfactants.

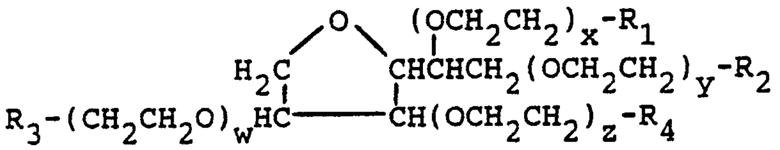
DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a light-sensitive non-silver photographic element including a support base and a hydrophilic layer coated thereon including an ionic dye-counter ion imaging combination dissolved in water-immiscible organic solvent droplets. The droplets are dispersed in the hydrophilic layer in reactive association with a sorbitan ester non-ionic surfactant having a HLB value in the range from 4 to 10.

The selection of the surfactant needed to make the oil ionic dye-counter ion dispersion and to keep it stable (free from crystallization) within the layer (including it) is critical not only to the stability of the dispersion but also to the sensitometric results obtained with such dye-ion imaging combination. The use of anionic and cationic surfactants has been found to result in poor sensitivity and high D_{min}. It is believed that they disrupt the ionic dye-counter ion reactive association which is the basis of the imaging process of interest to the present invention.

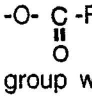
Non-ionic surfactants are believed to be particularly good aids for the ionic dye-counter ion imaging chemistry due to the fact that they do not apparently disrupt the necessary dye-activator salt. Within the class of non-ionic surfactants, it has been found that better results are obtained if the dispersion is made in the presence of a sorbitan ester non-ionic surfactant having a HLB value of 4 to 10.

Such sorbitan ester non-ionic surfactant compounds may be a sorbitan fatty acid ester non-ionic surfactant or a polyoxyethylene sorbitan fatty acid ester non-ionic surfactant, represented by the general formula (I) :



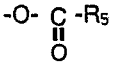
(I)

wherein w+x+y+z represents 0 to 30, preferably 5 to 20, and R_1, R_2, R_3 and R_4 each represents a hydroxy group or a



$-O-\underset{\underset{O}{\|}}{C}-R_5$

group wherein R_5 represents an aliphatic saturated or unsaturated carbon atom alyphatic chain of a fatty acid, preferably including 5 to 30 carbon atoms, such as lauric acid, myristic acid, palmitic acid, oleic acid, stearic acid, ricinoleic acid and the like, in which at least one of R_1, R_2, R_3 and R_4 represents a hydroxy group and at least one of R_1, R_2, R_3 and R_4 represents a



$-O-\underset{\underset{O}{\|}}{C}-R_5$

group, and the value of w+x+y+z and the nature and size of R_5 are chosen to get a HLB value of 4 to 10.

The sorbitan fatty acid ester non-ionic surfactants are, in general, manufactured by direct reaction of sorbitol with fatty acids under the influence of heat or acidic reagents or both, during which internal ether formation as well as esterification occurs. The sorbitan fatty acid esters resulting from simultaneous internal ether formation and esterification consist of components esterified to different extents (mono-, di- and triesters) as described by F. R. Benson in Nonionic Surfactants, edited by M. J. Schick, M. Dekker Inc. New York, 1967, pages 264-266.

The polyoxyalkylene sorbitan fatty acid ester non-ionic surfactants are, in general, manufactured by reaction of ethylene oxide with sorbitan fatty acid esters as described by F. R. Benson in Nonionic Surfactants, edited by M. J. Schick, M. Dekker Inc. New York, 1967, pages 270-272.

The following table reports sorbitan ester non-ionic surfactants for use in the present invention:

Chemical Name	w+x+y+z	HLB	Trade Name
Sorbitan oleate	0	4.3	SPAN™ 80
Sorbitan stearate	0	4.7	SPAN™ 60
Sorbitan palmitate	0	6.7	SPAN™ 40
Sorbitan laurate	0	8.6	SPAN™ 20
Polyoxyethylene sorbitan stearate	5	9.6	TWEEN™ 61

Such non ionic surfactants are to be used in the substantial or total absence of any anionic or cationic surfactants. Sorbitan esters, such as for example SpanTM-20, are highly preferred as leading to thermo-stable, well resolved (<1 µm) droplet dispersion of oil in gelatin, with the imaging chemistry located in the oil as desired. TergitolTM (e.g. TMN-10) non-ionic surfactants may be used but they give dispersions with medium to poor thermo-stability and larger droplets than attainable with sorbitan esters.

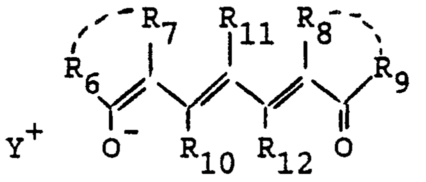
HLB (hydrophilic-lipophilic balance) is a measure of the emulsifying efficiency of a surfactant and is related to the polarity of the molecule, the least hydrophilic surfactants having low HLB numbers, and increasing HLB numbers corresponding to increasing hydrophilic character (for a detailed definition of HLB see M.J. Schick, Surfactants Science Series, Vol. 1 Nonionic Surfactants, Chapter 18, M. Dekker Inc. (New York), 1967).

Sorbitan esters (SPANTM) and polyoxyethylene sorbitan esters (TWEENTM) can be used in conjunction, taking care that the average of the two HLB values remains between 4 to 10.

The ionic dyes used may be either anionic and cationic, depending on the polarity of the active counter ion.

A preferred embodiment of the invention involves an anionic dye in reactive association with a positively charged counter ion, such as for example an iodonium$^+$ counter ion.

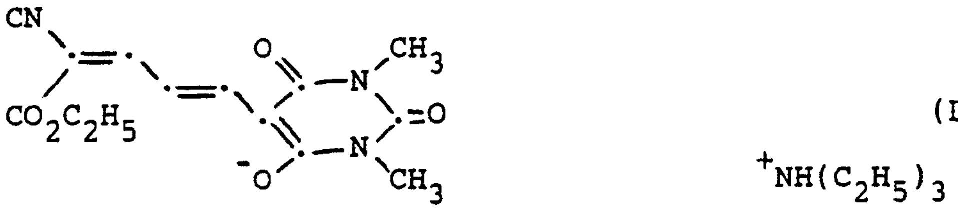
Particularly useful anionic dyes for use in this invention are oxonol dyes of the general formula (II):



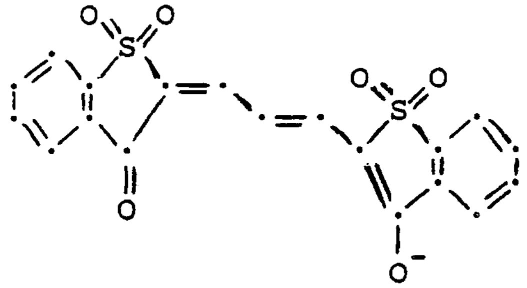
(II)

wherein R_6, R_7, R_8 and R_9 each represents 1 to 10 atoms chosen among carbon, hydrogen, nitrogen, oxygen or sulfur to form a substituent such as substituted or unsubstituted alkly group or aryl group (such as phenyl, naphthyl group) or heterocyclic group (such as pyridyl group) directly linked to the rest of the molecule or attached to the molecule through link groups such as oxygen, sulfur, carbonyl, sulfonyl, carbonamido, sulfonamido, ureido, carbonylester, carbamoyl, sulfamoyl, aminocarnonyl and aminosulfonyl, and the like, or other terminal groups, preferably electron-withdrawing groups, such as cyano, hydroxy, nitro and halogen (Cl, Br and F). R_6, R_7, R_8 and R_9 may be the same or different and are chosen to form a symmetrical or an unsymmetrical dye molecule. R_6 and R_7 and, respectively, R_8 and R_9 may be taken together to represent the C, H, N, O and S atoms to form a simple (5 or 6 atoms) or condensed (including 9 or 10 atoms) heterocyclic or alicyclic nucleus (such as barbituric acid, thiobarbituric acid, pyrazolone, oxindole, indandione, isoxazolone and 1,1-dioxo-3-oxothiophene). R_{10}, R_{11} and R_{12} each represents hydrogen, low alkyl groups (containing 1 to 5 carbon atoms), aryl groups (such as phenyl group), saturated and unsaturated heterocyclic groups (such as pyridine and pyrroline groups) or alicyclic groups having 5 or 6 carbon atoms (such as cyclopentane and cyclohexane) or atoms chosen within carbon, hydrogen, nitrogen, oxygen and sulfur to form a simple (including 5 or 6 atoms) or condensed (including 9 or 10 atoms) aromatic or heterocyclic or alicyclic nucleus (such as phenyl, piridyl, naphthalene groups). The substituents R_6, R_7, R_8, R_9, R_{10}, R_{11} and R_{12} are chosen to give dyes useful to the present invention as known in the art, preferably having no more than 40 carbon atoms. Y^+ represents a cation.

Examples of oxonol dyes include:

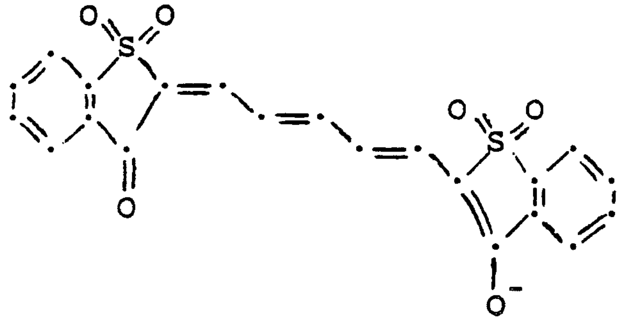


(Dye 1)



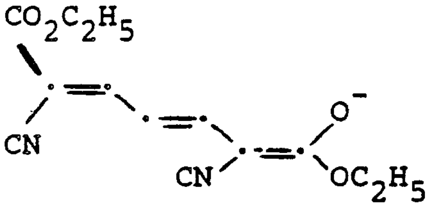
(Dye 2)

$^{+}NH(C_2H_5)_3$



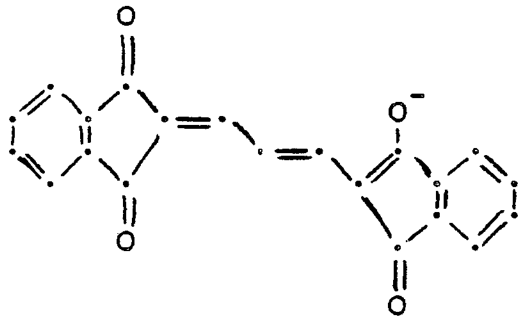
(Dye 3)

$^{+}MH(C_2H_5)_3$



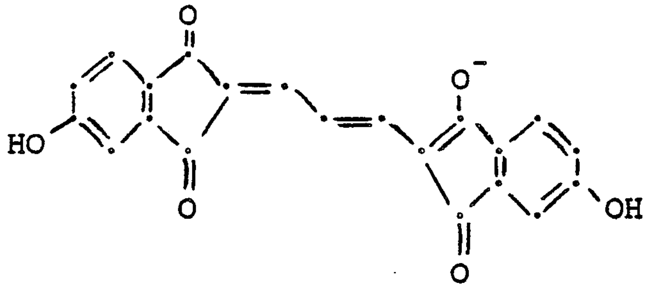
K^{+}

(Dye 4)



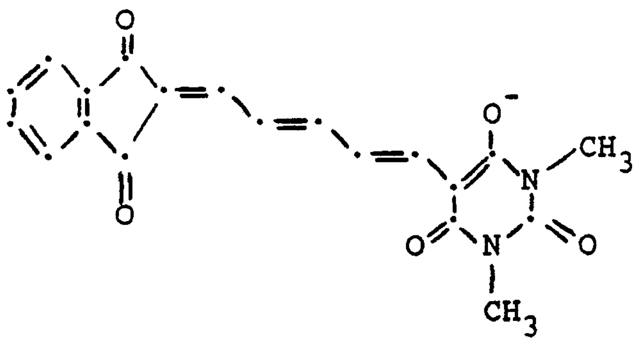
$^{+}NH(C_2H_5)_3$

(Dye 5)



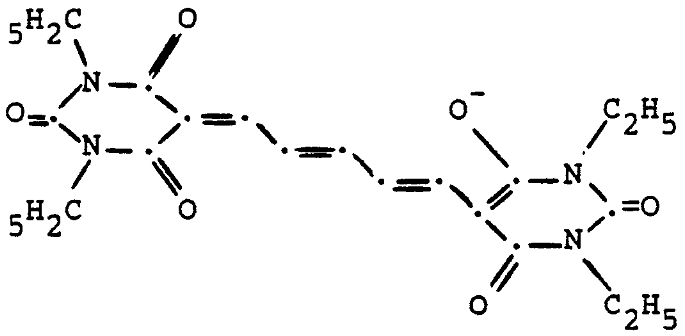
$^{+}NH(C_2H_5)_3$

(Dye 6)



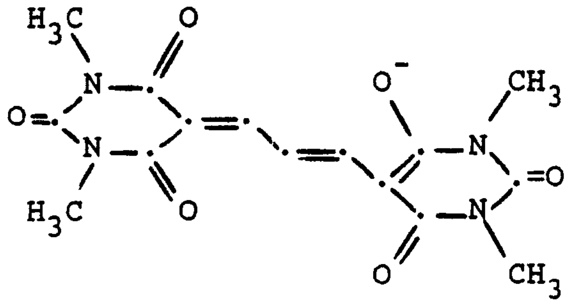
$^{+}NH(C_2H_5)_3$

(Dye 7)



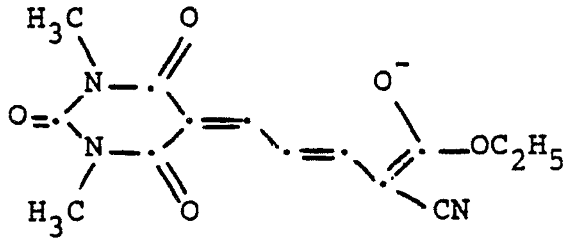
$^{+}NH(C_2H_5)_3$

(Dye 8)



$^{+}NH(C_2H_5)_3$

(Dye 9)

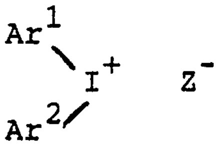


$^{+}NH(C_2H_5)_3$

(Dye 10)

As already said, a particular useful counter ion to be associated with a negatively charged dye is an iodonium^{+} counter ion of an iodonium salt. The iodonium salts that may be used in the imaging system are compounds consisting of a cation wherein a positively charged iodine atom bears two covalently bonded carbon atoms, and any anion. Preferably the acid from which the anion is derived has a pKa <5. The preferred compounds, as described in European patent application No.120,601, are diaryl, aryl/heteroaryl or diheteroaryl iodonium salts in which the carbon-iodine bonds are from aryl or heteroaryl groups. Aliphatic iodonium salts are not normally thermally stable at temperature above 0°C. However, stabilised alkyl phenyl iodonium salts such as those disclosed in Chem.Lett. 1982, 65-6 are stable at room temperature and may be used.

Suitable iodonium salts may be represented by the formula (III):

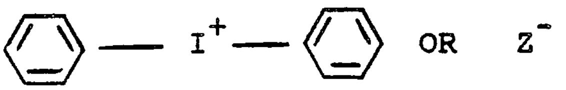


(III)

wherein Ar^1 and Ar^2 independently represent carbocyclic or heterocyclic aromatic-type groups generally having from 4 to 20 carbon atoms, or together with the iodine atom complete an "aromatic" heterocyclic ring (to the purposes of the present invention pyrazole, thiazole and furane are considered aromatic heterocyclic nuclei). These groups include substituted and unsubstituted aromatic hydrocarbon rings, e.g. phenyl or naphthyl, which may be substituted with alkyl groups, e.g. methyl, alkoxy groups, e.g. methoxy, butoxy, chlorine, bromine, iodine, fluorine, carboxy, cyano or nitro groups or any combination thereof. Examples of hetero-cyclic groups include thienyl, furanyl and pyrazolyl groups which may be substituted with similar substituents as described above. Condensed aromatic/hetero-aromatic groups, e.g. 3-indolinyl, may also be present.

Z^- represents an anion (such as, for example, Cl^-, I^-, Br^-, perfluoro(4-ethylcyclohexane)sulfonate, sulfate, methyl sulfate, methanesulfonate) which may be incorporated into Ar^1 or Ar^2.

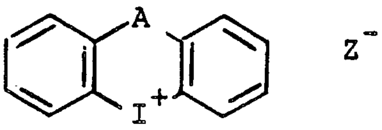
Preferably, Ar^1 and Ar^2 do not have more than two substituents at the α-positions of the aryl groups. More preferably, Ar^1 and Ar^2 are both phenyl groups containing no α substituents, such as in iodonium salts represented by the formula (IV):



(IV)

wherein R is an alkyl group having 1 to 20 carbon atoms, preferably having 1 to 5 carbon atoms, such as methyl, ethyl, iso-propyl or n-butyl. Z^- has the same meaning as in (III).

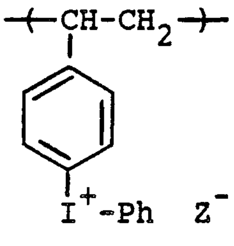
The α-positions of the aryl groups may be linked together to include the iodine atom within a ring structure, such as in iodonium salts represented by the formula (V):



(V)

in which A is an oxygen or sulphur atom. Z^- has the same meaning as in (III).

Other suitable iodonium salts include polymers containing units (VI)

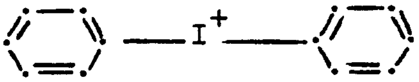


(VI)

in which Ph represents phenyl. Z^- has the same meaning as in (III).

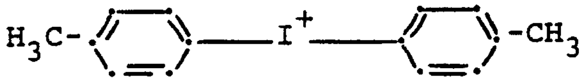
Examples of such polymers are disclosed in Yamada and Okowara,"Makromol.Chemie", 1972, Vol.152, 61-66. Examples of iodonium salts include:

Iodonium salt 1



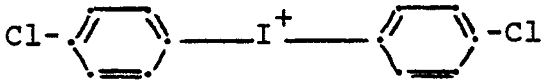
PF_6^-

Iodonium salt 2



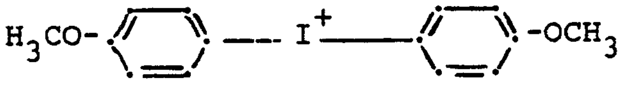
PF_6^-

Iodonium salt 3



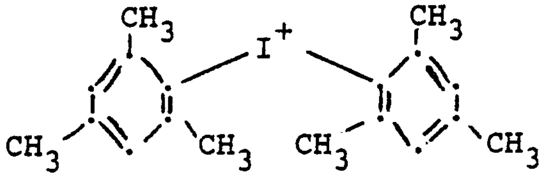
PF_6^-

Iodonium salt 4



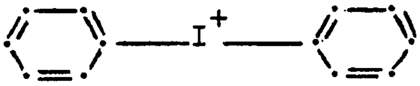
PF_6^-

Iodonium salt 5



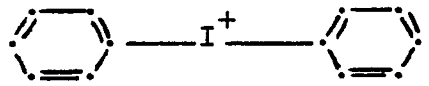
PF_6^-

Iodonium salt 6



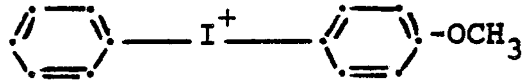
$C_6H_5SO_3^-$

Iodonium salt 7



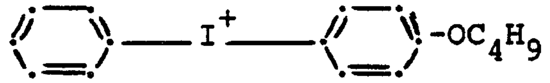
$CH_3-C_6H_5SO_3^-$

Iodonium salt 8



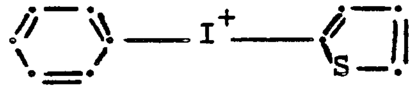
$CF_3CO_2^-$

Iodonium salt 9



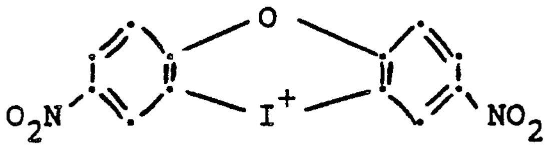
$CF_3CO_2^-$

Iodonium salt 10



$CF_3CO_2^-$

Iodonium salt 11



PF_6^-

The dye/iodonium system has its greatest sensitivity at the lambda$_{max}$ of the longest wavelenght absorbance peak. Generally, it is necessary to irradiate the system with radiation of wavelenght in the vicinity of this lambda$_{max}$ for bleaching to occur. Thus, a combination of coloured dyes may be used, e.g. yellow, magenta and cyan, in the same or different layers in an element and these can be selectively bleached by appropriate visible radiation to form a full color image. Monochromatic or polychromatic images may be produced by using the photosensitive materials with relatively short exposure times in daylight or sunlight or even artificial sources of light (e.g. fluorescent lamps or laser beam). The exposure time, for adequate results, for example when using an 0.5 kW tungsten lamp at a distance of 0.7 m, may be between 1 second to 10 minutes. In general, the weight ratio of bleachable dye to iodonium salt in the element is in the range from 1:1 to 1:50, preferably in the range from 1:2 to 1:10.

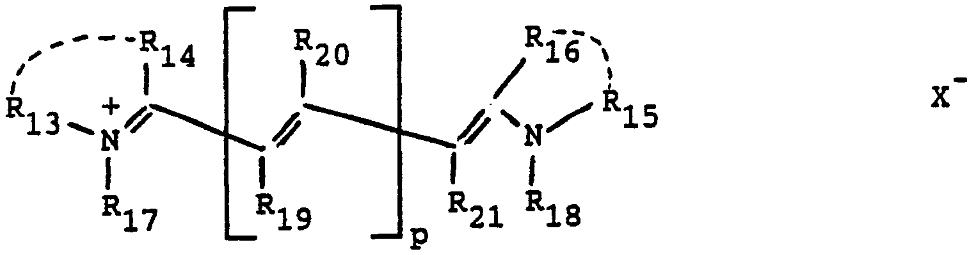
A preferred composition of the dye iodonium ion bleaching reaction is the combination of an oxonol dye anion with the activator iodonium cation to form an organic salt which is highly soluble in oils, such as di-butyl phthalate, di-butyl lauramide. The close reactive association of the sensitizing dye with the iodonium moiety ensures easy electron transfer from the dye to the iodonium moiety, as desired.

Another embodiment of the present invention comprises a cationic dye in reactive association with a negatively charged counter ion. In fact, as described in US patent No. 4,307,182, dye bleaching systems can give good results by using positively charged dyes in reactive association with a negatively charge counter-ion, such as a borate$^-$ counter ion.

The cationic dye to be used in reactive association with the borate$^-$ counter ion may be of any color and any chemical class. The dyes, of course, should not contain groups which would fix or desensitize the borate salts (e.g. carboxylic acid groups, sulfonic acid groups and readily reducible metal cations such as metal cations at least as readily reducible as ferric ion).

When the ionic dye is a cationic dye, the bleachable dyes may be selected from a wide range of known classes of dyes including methine, cyanine, carbocyanine, azomethine, styryl, xanthene, azine or rhodamine dyes.

Particularly useful cationic dyes are cyanine dyes of the general formula (VII):



wherein p is an integer of 0 to 5 and R_{13}, R_{14}, R_{15} and R_{16} each represents 1 to 10 atoms chosen among carbon, hydrogen, nitrogen, oxygen or sulfur to form a substituent such as substituted or unsubstituted alkly group or aryl group (such as phenyl, naphthyl group) or heterocyclic group (such as pyridyl group) directly linked to the rest of the molecule or attached to the molecule through link groups such as oxygen, sulfur, carbonyl, sulfonyl, carbonamido, sulfonamido, ureido, carbonylester, carbamoyl, sulfamoyl, aminocarbonyl and aminosulfonyl, and the like, or other terminal groups, preferably electron-withdrawing groups, such as cyano, hydroxy, nitro and halogen (Cl, Br and F). R_{13}, R_{14}, R_{15} and R_{16} may be the same or different and are chosen to form a symmetrical or an unsymmetrical dye molecule. R_{13} and R_{14} and, respectively, R_{15} and R_{16} may be taken together to represent the C, H, N, O and S atoms to form a simple (5 or 6 atoms) or condensed (including 9 or 10 atoms) heterocyclic nucleus, such as oxazoline, oxazole, benzoxazole, the naphthoxazoles (e.g. naphth{2,1-d}oxazole, naphth{2,3-d}oxazole and napth[1,2-d}oxazole), thiazoline, thiazole, benzothiazole, the naphthothiazoles (e.g. naphtho{2,1-d}thiazole), the thiazoloquinolines (e.g. thiazolo{4,5-b}quinoline), selenazoline, selenazole, benzoselenazole, the naphthoselenazoles (e.g. naphtho{1,2-d}selenazole), 3H-indole (e.g. 3,3-dimethyl-3H-indole), the benzimidazoles (e.g. 1,1-dimethylbenzimidazole), imidazoline, imidazole, benzimidazole, the naphthimidazoles (e.g. naphth{2,3-d}imidazole), pyridine and quinoline, which nuclei may be substituted on the ring by one or more of a wide variety of substituents, such as hydroxy, the halogens (e.g. fluoro, bromo, chloro and iodo), alkyl groups or substituted alkyl groups (e.g. methyl, ethyl, propyl, isopropyl, butyl, octyl, dodecyl, 2-hydroxyethyl, 3-sulfopropyl, carboxymethyl, 2-cyanoethyl and trifluoromethyl), aryl groups or substituted aryl groups (e.g. phenyl, 1-naphthyl, 2-naphthyl, 4-sulfophenyl, 3-carboxyphenyl and 4-biphenyl), aralkyl groups (e.g. benzyl and phenethyl), alkoxy groups (e.g. methoxy, ethoxy and isopropoxy), aryloxy groups (e.g. phenoxy and 1naphthoxy), alkylthio groups (e.g. ethylthio and methylthio), arylthio groups (e.g. phenylthio, p-tolylthio and 2-naphthylthio), methylenedioxy, cyano, 2-thienyl, styryl, amino or substituted amino groups (e.g. anilino, dimethylanilino, diethylanilino and morpholino), acyl groups (e.g. acetyl and benzoyl), and sulfo groups.

R_{17} and R_{18} can be the same or different and represent alkyl groups, aryl groups, alkenyl groups or aralkyl groups, with or without substituents (e.g. carboxymethyl, 2-hydroxyethyl, 3-sulfopropyl, 3-sulfobutyl, 4-sulfobutyl, 2-methoxyethyl, 2-sulfatoethyl, 3-thiasulfatoethyl, 2-phosphonoethyl, chlorophenyl and bromophenyl) having 1 to 10 carbon atoms.

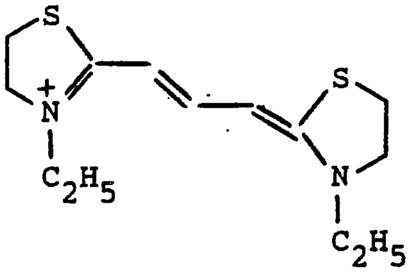
R_{19}, R_{20} and R_{21} each represents hydrogen, low alkyl groups (containing 1 to 5 carbon atoms), aryl groups (such as phenyl groups), saturated and unsaturated heterocyclic groups (such as pyridine and pyrroline groups) or alicyclic groups having 5 or 6 carbon atoms (such as cyclopentane and cyclohexane) or atoms chosen within carbon, hydrogen, nitrogen, oxygen and sulfur to form (when taken together) a simple (including 5 or 6 atoms) or condensed (including 9 or 10 atoms) aromatic or heterocyclic or alicyclic nucleus (such as phenyl, piridyl, naphthalene groups).

The substituents R_{13}, R_{14}, R_{15}, R_{16}, R_{17}, R_{18}, R_{19}, R_{20} and R_{21} are to give dyes useful to the present invention, as known in the art, preferably having no more than 40 atoms.

X^- represents an anion (such as, for example, Cl^-, I^-, Br^-, perfluoro(4-ethylcyclohexane)sulfonate, sulfate, methyl sulfate, methanesulfonate).

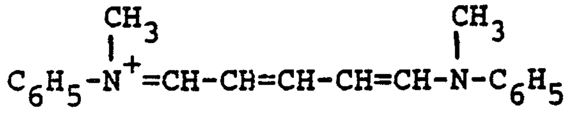
This class of dyes is very well known particularly in the silver halide photographic art and are the subject of numerous patents. General references to these dyes include "The Chemistry of Synthetic Dyes", K.Venkataraman ed., Academic Press,Vol.4 (1971) and "The Theory of the Photographic Process",T.H. James,ed.,MacMillan, Editions 3 and 4.

Examples of cyanine dyes include:



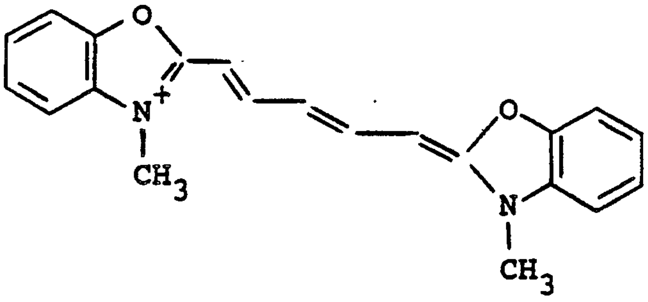
PECHS$^-$

(Dye 10)



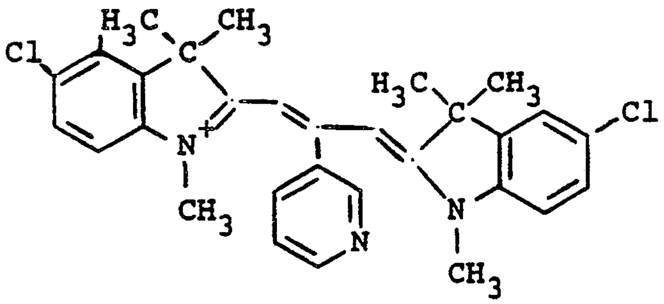
$$C_6H_5-\overset{CH_3}{\overset{|}{N^+}}=CH-CH=CH-CH=CH-\overset{CH_3}{\overset{|}{N}}-C_6H_5$$

PECHS$^-$ (Dye 11)



PECHS$^-$

(Dye 12)



PECHS$^-$

(Dye 13)

wherein PECHS is perfluoro(4-ethylcyclohexane)sulphonate.

As already said, particular useful counter ion to be associated with the positively charged dye is a borate$^-$ counter ion of a borate salt. Preferably, the borate salts that may be used in the imaging system are the tetra(aliphatic)borates, as described in US 4,307,182, wherein all of the carbon-to-boron bonds are from aliphatic groups.

Examples of borate salts include:

$(C_2H_5)_4N^+$ $(C_4H_9)_4B^-$	(Borate salt 1)
$(C_2H_5)_4N^+$ $(C_4H_9)_3(C_6H_5)B^-$	(Borate salt 2)
$(C_2H_5)_4N^+$ $(C_4H_9)(C_6H_5)_3B^-$	(Borate salt 3)
Na^+ $(C_6H_5)_4B^-$	(Borate salt 4)
$(C_2H_5)_4N^+$ $(C_4H_9)_3(CN)B^-$	(Borate salt 5)
$(C_2H_5)_4N^+$ $(COCH_3)_4B^-$	(Borate salt 6)
$(C_2H_5)_4N^+$ $(C_4H_9)_3(CH=CH_2)B^-$	(Borate salt 7)
$(C_2H_5)_4N^+$ $(C_4H_9)_3(CH_2\text{-}C_6H_5)B^-$	(Borate salt 8)
$(C_2H_5)_4N^+$ $(C_4H_9)_3(C\equiv CCH_3)B^-$	(Borate salt 9)

Imaging in the light sensitive dye/borate system is affected by irradiation. The radiation which is absorbed by the dye/borate system causes the dye to bleach. A positive image is then produced. The use of cationic dyes is believed to spectrally sensitize the borates to radiation absorbed by the dyes associated with the borate. These are not used as sensitizing dyes as used in photographic imaging systems (usually in ratios of 1/500 or 1/10000 of dye to light sensitive agents). These dyes are used in proportion of at least 1/10 to about 1/1 in ratio to the borate. Because the dye-borate system is molecularly spectrally sensitive, a multiplicity of colored dyes may be used (e.g. cyan, magenta and yellow) in the same or different layers.

"Reactive association", as used herein, is defined as such physical proximity between the compounds as to enable a chemical reaction to take place between them upon exposure to light.

By a suitable selection of dye, an element may be prepared which is sensitive to radiation of a selected wavelength band within useful ranges, such as 300 to 1100 nm, the particular wavelength and the width of the band depending upon the absorption characteristics of the dye. In general, where a dye has more than one absorption peak it is the wavelength corresponding to the longest wavelength peak at which one would choose to irradiate the element.

Elements intended for the production of images from radiation in the visible region (400 to 700 nm) will contain dyes which will bleach from a colored to a substantially colorless or very pale state. In practice, such bleachable dyes will undergo a change such that the transmission optical density at the $\text{lambda}_{\text{max}}$ will drop from 1.0 or more to less than 0.09, preferably to less than 0.05. The dyes will generally be coated on the support to provide an optical density of about 3.0 or more.

In the case of elements sensitive to ultraviolet radiation (300 to 400 nm), the dyes will not normally be colored to the eye and there may be no visible change upon exposure to ultraviolet and bleaching. The image-wise exposed elements may be used as masks for further ultraviolet exposure after fixing.

Infrared sensitive elements contain dyes having an absorption peak in the wavelength range 700 to 1100 nm. These dyes may also have absorption peaks in the visible region before and/or after bleaching. Thus as well as providing a mean for obtaining masks for subsequent infrared exposure in a similar manner to the ultraviolet masks, infrared sensitive elements may record a visible image upon image-wise exposure to infrared radiation.

The present invention also relates to a coating composition for the manufacture of a light sensitive non-silver photographic element which includes an ionic dye-counter ion imaging composition dissolved in a water immiscible organic solvent dispersed therein in the form of droplets associated with a non-ionic sorbitan ester surfactant compound having a HLB value of 4 to 10.

In another aspect, the present invention relates to a process for the manufacturing of a light sensitive non-silver photographic element which includes coating on a support base a composition substantially consisting of a hydrophilic binder having dispersed therein droplets of a water immiscible organic solvent including dissolved therein an ionic dye-counter ion imaging composition in the presence of a sorbitan ester surfactant compound having a HLB value of 4 to 10.

Typically, the process of incorporating hydrophobic additives, such as hydrophobic dye-counter ion combination agents, into hydrophilic colloid components layers of photographic materials (such as light sensitive layers, protective layers, intermediate layers and the like), consists of incorporating into hydrophilic colloid coating compositions of said layers the hydrophobic additives themselves in the form of a dispersion of fine droplets consisting of a water-immiscible high boiling organic solvent in which said hydrophobic additives have been dissolved.

Generally, according to said dispersion technique, the hydrophobic photographic additives are dissolved in water-immiscible high boiling organic solvents (also called in the art permanent solvents, crystalloidal solvents, oil solvents, oil-formers and the like) and the resulting organic solution is added to an aqueous composition containing the hydrophilic colloid (gelatin) and a dispersing agent (surfactant). The mixture is then passed through a homogeneizing apparatus (colloidal mill) to form a dispersion of fine droplets of said organic solvent comprising the hydrophobic photographic additives. The obtained dispersion is then mixed with the hydrophilic colloid composition (light sensitive gelatin composition or other gelatin composition) which is used to form (by coating) the photographic layer. The obtained photographic layer includes the additive dispersed therein.

Organic solvents for dispersing hydrophobic compounds are desired to meet several requirements. They have to possess an excellent dissolving power towards said additives, to keep the fine droplets stably dispersed, to have a refractive index which is as close as possible to that of the hydrophilic colloid wherein they are dispersed, and not to deteriorate the physical properties of the layers wherein they are incorporated. Moreover, said organic solvents have to not negatively affect the photographic properties of the materials wherein they are used to disperse photographic additives. Organic solvents may be selected from esters of carboxylic acid, phosphate esters, carboxyl amides, ethers and substituted hydrocarbons. Specific examples are di-n-butyl phthalate, 2(ethyl-hexyl)phthalate, di-octyl phthalate, diisodecyl phthalate, di-(methoxyethyl) phthalate, N-N-diethyl lauramide, di-butyl lauramide, butyl acetanilide, tricresyl phosphate, tributyl phosphate, tri (butoxy-ethyl) phosphate, di-butyl sebacate, di-octyl sebacate, etc.

The amounts of high boiling solvents used according to this invention for dispersing hydrophobic additives can vary according to the used additive. It is, however, undesiderable to use large amounts of such solvents, because large excess of solvents may sometimes deteriorate the physical properties of the photographic layers. Accordingly, it is normal practice to use the high boiling solvents in a weight ratio to each additive in the range 01 to 8.0, preferably in the range 0.3 to 3.0.

A low-boiling solvent or water-soluble high-boiling solvent is sometimes advantageously used along with the water-insoluble high-boiling solvent as mentioned above for dissolving the ionic dye-counter ion combination, e.g., propylene carbonate, ethyl acetate, butyl acetate, ethyl propionate, sec-butyl alcohol, tetrahydro-furan, cyclohexanone, dimethylformamide, diethylsulphoxide and 2-methoxy ethanol. Auxiliary low boiling organic solvents are for example described in U.S. patents Nos. 2,801,170; 2,801,171; 2,835,579 and 2,949,360.

The bleachable dye and counter ion salt may be applied to the support in a binder. Suitable binders are transparent or translucent, are generally colourless and include natural polymers, synthetic resins, polymers and copolymers, and other film forming media. The binders may range from thermoplastic to highly cross-linked, and may be coated from aqueous or organic solvents or emulsions.

Gelatin is the preferred hydrophilic colloid for use in the present invention. However, other water-soluble colloidal substances or mixture thereof can also be used. Exemplary hydrophilic colloidal substances include gelatine derivatives, such as phthalated gelatin and acetylated gelatine, cellulose derivatives, such as carboxymethyl cellulose, starch, casein, zein, synthetic hydrophilic colloids such as polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of acrylic acid esters, acrylonitrile and acrylamides, etc.

The amount of gelatin used in practice depends on the dispersing solvent amount and the coating thickness required. It is advantageously used in the amount of 2.5 to 5% by weight of whole dispersion.

Suitable supports include transparent film, e.g. polyester, paper e.g. baryta-coated photographic paper, and metallised film. Opaque vesicular polyester films are also useful.

EXAMPLE 1

The following stock emulsion was prepared.

Yellow dyes represented by the formulas (1) and (4) (2.0 g and 1.6 g) were dissolved in a mixture of 24 ml of DEL (diethyl lauramide), 4 ml of dimethyl formamide (DMF) and ethanol (30 ml) at 50 °C. To this solution, in red light, was added the iodonium salt (9) (5.2 g). The resulting solution was dropwise added to 200 ml of 10% aqueous gelatin while stirring with a high speed rotating mixer to effect dispersion. The dispersion was continued for 5 minutes, after which time 136 ml water was added and dispersion maintained for 3 minutes. This stock emulsion is used immediately, because although initially the emulsion is well formed with <0.1 µm droplets, it is not stable after 12 hours at room temperature. Separation of the oil is observed.

a) Standards without any surfactant.

A 100 ml aliquot of above stock solution was placed at 40 °C for 24 hours and its oil/gelatin dispersion stability monitored by optical observation of the droplets between glass plates.

The emulsion was found to separate large oil drops after 24 hours.

The emulsion was conventionally coated onto subbed polyester and dried for 1 hour at 40 °C in the dark. The resulting yellow coating was analysed by monitoring the sensitivity of the yellow dye bleach at 460 nm. The time taken to bleach the dye by D_{max}-1 speed point by known amount of light at 460 nm was obtained. There was no unbleached dye, i.e. D_{min} = 0.05.

b) With the addition of an anionic surfactant.

As above, but adding 7 ml of 10% aqueous anionic Hostapur™ surfactant to 100 ml of the stock dispersion. The stability was monitored for 24 hours/40 °C. A sample of the obtained coated film was analyzed as above for sensitivity and D_{min}.

c) With the addition of non-ionic surfactant.

As in case b), but using non-ionic TergitolTM TMN-4 surfactant (10%aqueous, 7 ml).

d) With the addition of non-ionic surfactant.

As in case b), but using non-ionic TergitolTM TMN-10 surfactant (10%aqueous, 7 ml).

The stock dispersion is completely destroyed with considerable oil separation.

e) With the addition of non-ionic surfactant.

As in case b), but using Span^{Tm} 20, 0.2 g for 100 ml dispersion.

The results of the test are shown in the following table 2:

Dispersion	Stability 24 hrs/40° C	Time (Secs) (D_{max}-1)	Unbleached dye (D_{min})
Case a)	Oil Separation	25	0.05
Case b)	Good stability	40	0.39
Case c)	Good stability	30	0.10
Case d)	Considerable oil separation	--	-
Case e)	Good stability	23	0.10

As we can see in table 2, the best dispersion stability, high speed and low D_{min} is achieved in the case e), corresponding to the use of the non-ionic SpanTM 20 type surfactant.

The HostapurTM surfactant of case b) is an anionic surfactant. It gives a good stability but the values of D_{max} and D_{min} obtained by the use of such a type of surfactant are worse than the values obtained without the use of any surfactants.

The TergitolTM TMN-4 and TergitolTM TMN-10 surfactants of, respectively, cases c) and d) are non-ionic surfactants. By the use of TergitolTM TMN-4 a good stability is obtained and the values of D_{max} and D_{min} are better than the values obtained in case b) (by the use of an anionic surfactant).

EXAMPLE 2

1.3 g of the iodonium salt (9) was added under diminuished red light to a solution obtained by heating to 56° C ± 2° of 0.5 g of yellow dye (10) and 0.4 g of yellow dye (4), 6 ml of DEL, 1 ml of DMF, 7 ml of ethanol and 0.2 g of Sorbitan monolaurate.

The resulting solution was added to 50 ml of an aquecus solution kept at 45° C and containing 5 g of gelatine. The resulting mixture was stirred for 5 minutes in a high speed rotary mixer to effect dispersion.

To the whole dispersion thus formed was added 33.91 ml of water; this was stirred for an additional 3 minutes, then observed by means of an optical microscope. This is a process for producing a unique combination of organic solvent (DEL) and non-ionic surfactant, without any anionic surfactant, permitting the formation of thermostable, well resolved oil-in-gelatin dispersion.

The dispersion was stable and it was observed that no agglomeration of the particles, growth of the particles or crystallisation occurred.

EXAMPLE 3

To a solution obtained by heating a mixture of 0.5 g of magenta oxonol dye (6), 6 ml of DEL, 1 ml of DMF, 7 ml of ethanol and 0.2 g of SpanTM 20, was added under diminuished red light 0.6 g of the iodonium salt (9).The resulting solution was added to 85 ml of an aqueous solution kept at 45° C and containing 5 g of gelatin, and the resulting mixture was treated for 5 minutes by means of 20 kHz electromagnetic ultrasonic generator (Sonifer™ Mod. B-12 of Branson Co.). The dispersion showed good drop size distribution curve (DSDC) and an excellent thermostability; no crystals were observed.

EXAMPLE 4

0.5 g of the oxonol salt of formula (3) was dissolved by heating in a mixture of 6 ml of DEL, 1 ml of DMF, 7 ml ethanol and 0.2 of non-ionic surfactant (Span™ 20). Under a diminuished yellow-green light, 0.6g of iodonium salt (9) was added and the resulting solution was stirred by Silverson into 50 ml of 10% aqueous gelatin kept at 45° C.

After homogenising for 10 minutes, additional 35 ml of water was poured in and subjected to Siverson homogenisation for a further 2 minutes. The whole dispersion was thus prepared, showed good DSDC and stability without any tendency to crystallise.

Claims

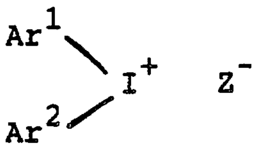
1. A light-sensitive non-silver photographic element including a support base and a hydrophilic layer coated thereon including an ionic dye-counter ion imaging combination dissolved in water-immiscible oil solvents dispersed therein in reactive association with a non-ionic sorbitan ester surfactant compound having an HLB value in the range 4 to 10 in absence of anionic surfactants.

2. The light-sensitive non-silver photographic element of claim 1 in which said sorbitan ester compound is a polyoxyethylene derivative thereof.

3. The light-sensitive non-silver photographic element of claim 1 wherein said ionic dye-counter ion imaging combination is an anionic dye reactively associated with an iodonium counter ion.

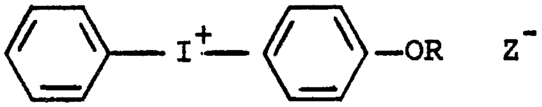
4. The light-sensitive non-silver photographic element of claim 3 wherein said anionic dye is an oxonol dye.

5. The light-sensitive non-silver photographic element of claim 3 wherein said iodonium counter ion is represented by the formula :



wherein Ar^1 and Ar^2 independently represent carbocyclic or heterocyclic aromatic-type groups having from 4 to 20 carbon atoms, or together with the iodine atom complete a heterocyclic aromatic ring, and Z^- represents an anion which may be present in Ar^1 or Ar^2.

6. The light-sensitive non-silver photographic element of claim 3 wherein said iodonium counter ion is represented by the formula :



wherein R is an alkyl group having 1 to 20 carbon atoms and Z^- represents an anion.

7. The light-sensitive non-silver photographic element of claim 1 wherein said ionic dye-counter ion imaging combination is a cationic dye reactively associated with a borate counter ion.

8. The light-sensitive non-silver photographic element of claim 7 wherein said cationic dye is a cyanine dye.

9. The light-sensitive non-silver photographic element of claim 8 wherein said borate counter ion is a tetra(aliphatic)borate.

10. The light-sensitive non-silver photographic element of claim 1 wherein said oil solvents are esters of carboxylic acid, phosphate esters, carboxyl amides, ethers or substituted hydrocarbons.

11. A coating composition for the manufacture of a light sensitive non-silver photographic element which includes an ionic dye-counter ion imaging composition dissolved in a water immiscible organic solvent dispersed therein in the form of droplets associated with a non-ionic sorbitan ester surfactant compound having a HLB value of 4 to 10.

12. A process for the manufacturing of a light sensitive non-silver photographic element which includes coating on a support base a composition substantially consisting of a hydrophilic binder having dispersed therein droplets of a water immiscible organic solvent including dissolved therein an ionic dye-counter ion imaging composition in the presence of a sorbitan ester surfactant compound having a HLB value of 4 to 10.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 89 10 7013

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)
A	GB-A-1 460 894 (AGFA-GEVAERT) * Whole document * ---	1-12	G 03 C 7/02
A	EP-A-0 109 773 (MINNESOTA MINING AND MANUFACTURING CO.) * Whole document * ---	1-12	
A	US-A-3 676 141 (H. HARA et al.) * Column 1, line 1 - column 3, line 75; column 6, lines 1-23; column 10, lines 27-73 * ---	1-12	
A,D	US-A-3 860 425 (Y. ONO et al.) * Column 1, line 1 - column 11, line 26; column 22, line 44 - column 23, line 66 * -----	1-12	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	04-09-1989	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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