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(54) Photograhic material with effeciently used non-sensitizing dyes.

(57) Particular non-sensitizing dyes which are capable of forming an inclusion complex or clathrate with a soluble cyclodextrine compound, preferably a partially methylated cyclodextrin, show an increased extinction compared to the non-complexed dye, and, as a consequence, can be more effectively used as a filter-, acutance-, or anti-halation dye in a hydrophilic layer of a photographic material.

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(3.10/3.09/3.3.4)

1. Field of the invention.

The present invention relates to a photographic silver halide material containing a particularly efficient type of non-sensitizing dye.

2. Background of the invention.

Light-absorbing dyes incorporated in silver halide photographic materials can accomplish a variety of goals, including their use as filter dyes, acutance dyes or anti-halation dyes.

When present in a non-photosensitive top layer or intermediate layer they typically serve as filter dyes eliminating an unwanted part of the light spectrum of the exposure source. A well-known example is the yellow filter layer usually present in colour photographic materials in order to prevent blue light from reaching the green sensitive and red sensitive layers. Another example is formed by UV-absorbing compounds, usually present in the top protective layer, which prevent photochemical deterioration of the image dyes formed by colour development. Examples of useful UV-absorbers include the cyanomethyl sulphone-derived merocyanines of US-P 3,723,154, the thiazolidones, benzotriazoles and thiazolothiazoles of US-P 2,739,888, 3,253,921, 3,250,617 and 2,739,971, the triazoles of US-P 3,004,896, and the hemioxonols of US-P 3,125,597.

On the other hand light-absorbing dyes when present in the emulsion layer can serve as so-called "acutance dyes" or "screening dyes" improving the image sharpness by reducing the sidewise scattering of light by the emulsion grains.

In a third application light-absorbing dyes act as "anti-halation dyes" improving the image sharpness by diminishing the upward reflection of light by the support into the emulsion layer. For this purpose the dye can be incorporated in an undercoat, being a non-photosensitive layer between the emulsion layer and the support, or it can be incorporated in the base itself, or preferably, it can be present in one or more backing layers of the photographic material.

Useful dyes absorbing in the visible spectral region include, for instance, the coloured pigments of US-P 2,697,037, the pyrazolone oxonol dyes of US-P 2,274,782, the styryl and butadienyl dyes of US-P 3,423,207, the diaryl azo dyes of US-P 2,956,879, the merocyanine dyes of US-P 2,527,583, the merocyanine and oxonol dyes of US-P 3,486,897, US-P 3,652,284 and 3,718,472, and the enaminohemioxonol dyes of US-P 3,976,661. Absorbing dyes can be added as particulate dispersions as disclosed in US-P 4.092,168, EP 0 274 723 and EP 0 299 435.

Infra-red absorbing dyes are described in EP 0 251 282, in EP 0 288 076, and in US-P 4,839,265.

Dyes absorbing in the red spectral region of the di- or triphenylmethane type, some of which bear an electron-withdrawing group, are disclosed in e.g. GB 769,749, US 2,282,890, DE 1,038,395, FR 2,234,585, JP-A-59-228250, US 2,252,052 and A. Guyot, Compt.Rend. Vol. 114 (1907) p. 1120. Some of the compounds disclosed contain one or more water-solubilizing groups.

Light-absorbing dyes must fulfil a number of strict requirements. They must rinse out or decolourize as completely as possible during photographic processing in order to minimize unwanted residual dye stain. When washed out they or their reaction products should not deteriorate the physical or sensitometric properties of the photographic material during prolonged continuous processing. Moreover, in order to be effective during exposure, the spectral characteristics of incorporated anti-halation dyes or acutance dyes should match as good as possible the spectral sensitivity distribution of the emulsion layer. In its turn this spectral sensitivity distribution has to be tuned to the spectral characteristics of the exposure source.

Exposure sources can radiate a continuous extended spectrum such as natural daylight in the case of conventional photography or artificial tungsten light in the case of cinematographic recording. On the other hand they can emit only one particular wavelength or a limited set of discrete wavelengths such as it the case with lasers and light-emitting diodes. In recent years lasers are increasingly used as exposure source for phototype- and image-setting materials and for radiographic monitoring photography. Examples of such lasers include Ar ion lasers emitting in the blue spectral region, HeNe lasers emitting in the red spectral region, and laserdiodes emitting in the near infra-red and recently also in the far red spectral region. Any filter dye, acutance dye or anti-halation dye must be chosen so that its spectral characteristics matches with the exposure source in question.

The problem can arise that when a dye is chosen with the proper wavelength distribution its extinction coefficient is too low. In this case too high an amount of dye per m^2 must be incorporated in the hydrophilic photographic layer in question. This can make the coating composition uncoatable or it can render the coated layer too thick so that the developability and/or drying characteristics of the complete photographic material become impaired. To put the problem more general there is a permanent need for new methods for increasing the efficiency of non-sensitizing dyes.

It is an object of the present invention to provide a photographic material containing a non-sensitizing dye with increased extinction coefficient at the useful wavelength.

It is a further object of the present invention to provide a photographic material with improved sharpness characteristics.

It is still a further object of the present invention to provide a photographic material with very low residual colour stain after processing.

3. Summary of the invention.

The objects of the present invention are realized by providing a photographic material comprising a support, at least one silver halide emulsion layer, and optionally one or more other hydrophilic layers, characterized in that at least one of said layers contains a cyclodextrin compound having a water-solubility of at least 10 g/100 ml, and a non-sensitizing dye capable of forming a clathrate with said cyclodextrin compound.

It was found unexpectedly that due to clathrate formation between a sufficiently soluble cyclodextrin and a suitable non-sensitizing dye spectacular increases in extinction coefficient could be realized. Also unexpectedly photographic samples according to the invention showed a very low residual stain after processing.

A preferred cyclodextrin compound obeying the condition of sufficient water-solubility is a partially methylated cyclodextrin (PMCD).

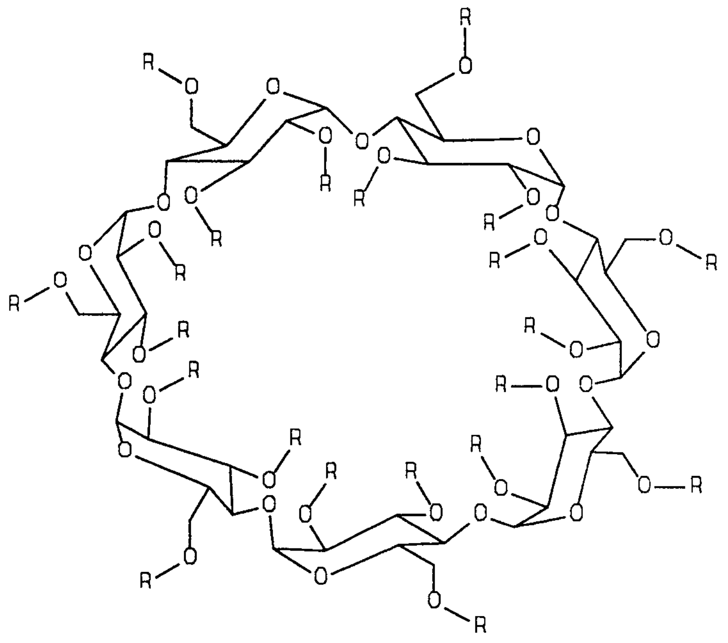
4. Detailed description of the invention.

Cyclodextrins are ring-shaped closed molecular structures composed of 6 glucose units in the case of α-cyclodextrin, 7 glucose units in the case of β-cyclodextrine and 8 glucose units in the case of γ-cyclodextrin. Supra-molecular structures known as inclusion complexes or "clathrates" of cyclodextrins are also known for long time. Teachings on clathrates can be found e.g. in F. Cramer, "Einschlus Verbindungen", Springer (1954), or M. Haga, "Clathrate Inclusion Compounds", Reinheld (1962).

Of the cyclodextrins only the β-variant is readily commercially available, but its water-solubility is too low (1.85 g/l) and that of its known clathrates is even lower so that it cannot be useful for the practice of this invention. Compounds that can be effectively considered are cyclodextrin derivatives, branched cyclodextrins and cyclodextrin polymers, such as the ones mentioned in e.g. EP 0 554 000, provided they comply with the restriction of a water-solubility of at least 10 g/100 ml.

Known cyclodextrin derivatives include compounds the hydroxyl group(s) of which are etherified, esterified or aminated. Such cyclodextrin derivatives are described in detail in M.L. Bender and M. Komiyama, "Cyclodextrin Chemistry", Shrupringer-Ferlarg (1978).

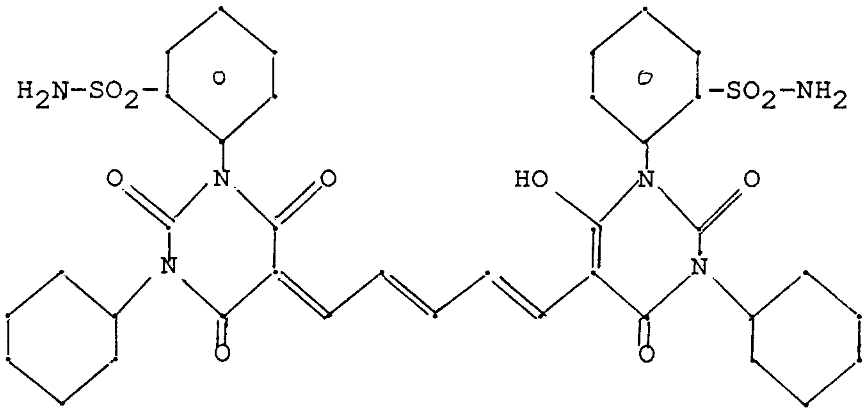
Preferred compounds are the etherified cyclodextrin derivatives, which show an increased water-solubility. Most preferred compounds for the practice of this invention are β-cyclodextrin derivatives where the hydroxyl groups at the second and sixth position are methylated or partially methylated, at least to such a degree that the condition of sufficient water-solubility is met. Such compounds can be represented by the following formula in which R is partially methyl and partially hydrogen:



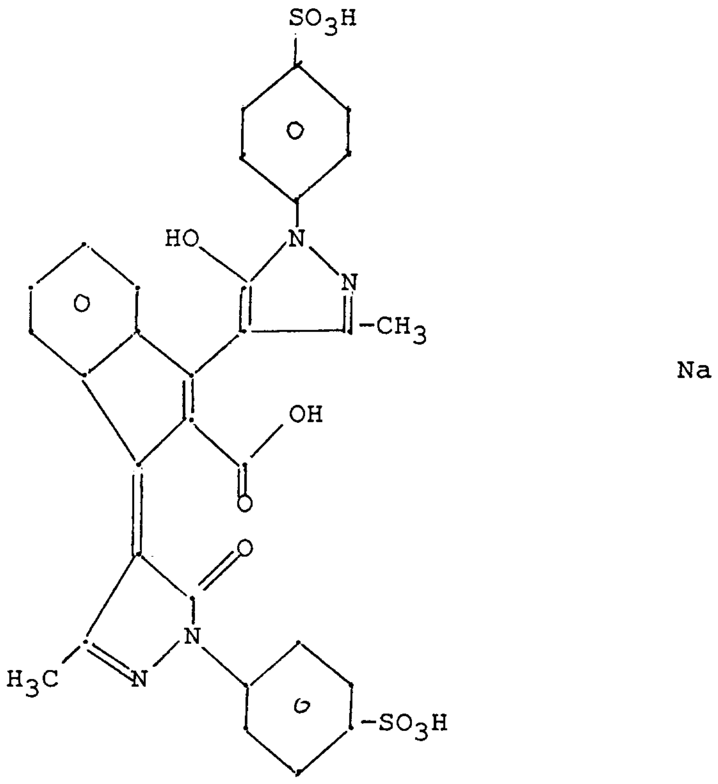
A commercially available example of such a compound, most preferred in connection with this invention, is partially methylated β-cyolodextrin (PMCD) marketed by Ringdex Co (16 rue Ballu, Paris, France). This substance has a methylation degree between 62 and 78 %, and a water solubility of more than 70 % (weight/volume). Furtheron it has a good solubility in currently used organic solvents.

As to the non-sensitizing dye for use in the photographic material of the present invention in principle any dye can be chosen provided it is capable to form a clathrate with a cyolodextrin compound. Self-evidently this implies a sufficient solubility in an hydrophilic medium such as a gelatinous coating solution. The possibility of forming a clathrate is difficult to predict solely on basis of chemical class because it will rather depend on molecular architecture if a given compound will be able to form an inclusion complex in the molecular cavity of cyclodextrin. In principle such a dye can be selected from any disclosure on non-sensitizing soluble dyes, such as from the references cited in the Background section and from more recent disclosures such as Unexamined Japanese Patent Publications 02-089051, 02-089046, 02-149842, 01-224749, 02-212833, 02-302752, 02-302751, 02-165135, 02-287347, 02-108040, 02-259753, 02-266348, 02-28640, and US-Patents 5,173,395, 5,206,125, 5,153,114, 5,204,231 and EP 0 539 978.

Most useful dyes include following compounds:



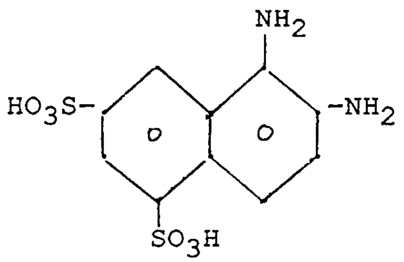
ID-1



ID-2

On forming a clathrate with PMCD these particular dyes give rise to a spectacular increase in extinction in vitro or in a coated hydrophilic layer. When coated in the backing layer of a photographic material sensitized in the region of maximal wavelength of the dye and its clathrate an increase in sharpness is obtained due to the improved anti-halation. This will be illustrated in the examples furtheron.

The combination of PMCD and ID-2 can constitute an interesting alternative for the well-known and commercially used non-sensitizing control dye, not capable of forming a clathrate, having following formula (CD-1), which shows some disadvantages, a.o., a low extinction coefficient, problems with hardening, viscosity fluctuations and iron sludge.



Fe, K

CD-1

Depending on its use as filter dye, acutance dye or anti-halation dye, the clathrate formed by the cyclodextrine compound and the non-sensitizing dye is incorporated in the appropriate emulsion layer, intermediate layer or backing layer. The clathrate can preferaby be formed in situ in the coating solution itself simply by the combined addition of dye and cyclodextrin. In a preferred embodiment of the present invention the clathrate serves as anti-halation dye and is present in a backing layer.

The type and application of the photographic material of the present invention is not specifically limited and can include graphic arts materials such as recording materials for the ouput of scanners, phototypesetters and imagesetters, duplicating materials, radiographic recording and hard-copy materials, diffusion transfer materials, and black-and-white or colour recording or print materials for general photography or cinematography.

In a preferred embodiment the photographic material is a near infra-red sensitive material, e.g. an image-setting material, since the best results were obtained with a clathrate derived from a dye (ID-2) absorbing in the far red and near infra-red region (see examples furtheron).

The halide composition of the silver halide emulsion(s) incorporated in the photosensitive emulsion layer(s) is not specifically limited and may be any composition selected from silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide.

The formation of the silver halide grains incorporated into the photosensitive emulsion layer occurs according to well-known conventional techniques. They can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method. The resulting silver halide particles may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms. The silver halide grains may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell which may have different halide compositions and/or may have undergone different modifications such as the addition of dopes. Besides having a differently composed core and shell the silver halide grains may also comprise different phases in between.

The average size of the silver halide grains may range from 0.05 to 1.0 µm, preferably from 0.2 to 0.5 µm. The size distribution of the silver halide particles of the photographic emulsion can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

The silver halide emulsion can be chemically ripened as described i.a. in "Chimie et Physique Photographique" by P. Glafkidès, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968) . As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur, e.g., thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors, e.g., tin compounds as described in GB 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. In a preferred embodiment conventional gold-sulphur ripening agents are used.

The silver halide emulsion(s) can be appropriately spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes.

The silver halide emulsion may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo[1,5-a]pyrimidines as described in US 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are metal salts such as, e.g., mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chapter VI.

The fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the ripening thereof and mixtures of two or more of these compounds can be used.

Besides the silver halide another essential component of a light-sensitive emulsion layer is the binder. The binder is a hydrophilic colloid, preferably gelatin. This gelatin can be lime-treated or acid-treated gelatin. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966). The gelatin can contain calcium or can be substantially free of calcium. Gelatin can, however, be replaced in part or integrallly by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinylpyrrolidone, polyvinylimidazole, polyvinylpyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g., other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkylcellulose, carboxymethylcellulose, phtaloylcellulose, and cellulosesulphates.

The binders of the photographic element, especially when the binder is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulphone type, e.g., 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes, e.g., formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds, e.g., dimethylolurea and methyloldimethylhydantoin, dioxan derivatives, e.g., 2,3-dihydroxy-dioxan, active vinyl compounds, e.g., 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952.

The photographic emulsion can be coated on a support by means of any of the conventional coating techniques, e.g. dip coating, air-knife coating, extrusion coating, slide-hopper coating and curtain coating.

The photographic material may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides, e.g., polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkyl aryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkylsulphonic acids, aminoalkyl sulphates or phosphates, alkylbetaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes, e.g., as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics, e.g., higher contrast, sensitization, and development acceleration.

The photographic element of the present invention may further comprise various other additives such as, e.g., compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents and plasticizers.

Suitable additives for improving the dimensional stability of the photographic element are i.a. dispersions of a water-soluble or hardly soluble synthetic polymer, e.g., polymers of alkyl (meth)acrylates, alkoxy (meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, α,β-unsaturated dioarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrenesulphonic acids.

The support of the photographic material may be opaque or transparent, e.g., a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an α-olefin polymer, e.g., a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support, e.g., cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinyl chloride film or poly-α-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer.

The photographic material according to the present invention has to be exposed and processed according to its specific design and application. In case of the preferred embodiment of an infra-red sensitive image-setting material the exposure source is a laserdiode and the material is conventionally black-and-white processed.

The present invention is illustrated by the following examples without however being limited thereto.

EXAMPLES

EXAMPLE 1

- in vitro experiments

Of dyes ID-1, ID-2 and CD-1 an aqueous solution containing 5 mg/l was made and the absorption spectrum was recorded from 200 to 800 nm. Then to 3 ml of this solution 50 mg of solid PMCD, marketed by Ringdex, was added and the mixture was shaken gently until a homogeneous solution was obtained. Then the absorption spectra were measured again. Table 1 shows the relative extinction change (% Δ) between before and after the addition of the cyclodextrin derivative at the respective absorption peak(s) (λ_{max}) of the dyes. The position of λ_{max} itself does not change substantially.

TABLE 1

dye	λ_{max}	% Δ of extinction
ID-1	590 nm	+21 %
ID-2	686 nm 758 nm	+58 % +146 %
CD-1	710 nm	no change

The table shows the raise in extinction of the dyes capable of forming a clathrate with PCMD. Especially for ID-2 which shows two absorption peaks the increase is remarkable.

EXAMPLE 2

- evaluation in a backing layer

Three samples of a first backing layer were coated. The coating solution of the first sample contained 54 g of gelatin, 100 ml of a 2,83 % solution of dye ID-2, and suitable amounts of colloidal silica, a conventional wetting agent and a conventional hardening agent. The coating solution of the second sample additionally contained 40 ml of a 10 % aqueous solution of PMCD, and the coating solution of the third sample contained 125 ml of said same solution. The three solutions were coated at a gelatin coverage of 2.16 g/m^2 onto a polyethylene terephthalate support. Then the three samples were overcoated with an identical second backing layer containing gelatin, a matting agent and several wetting agents, at a gelatin coverage of 0.98 g/m^2. Table 2 shows the densities of the coated layers at the absorption peaks of ID-2.

TABLE 2

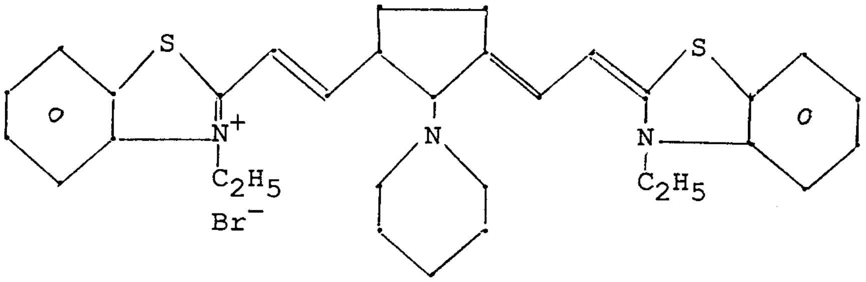
sample No.	λ_{max}^1	D at λ_{max}^1	λ_{max}^2	D at λ_{max}^2
1	696 nm	0.259	760 nm	0.246
2	694 nm	0.332	758 nm	0.331
3	690 nm	0.435	758 nm	0.483

The results of table 2 clearly illustrate the increase in density for the same amount of dye due to the formation of the inclusion complex with the cyclodextrin derivative.

EXAMPLE 3

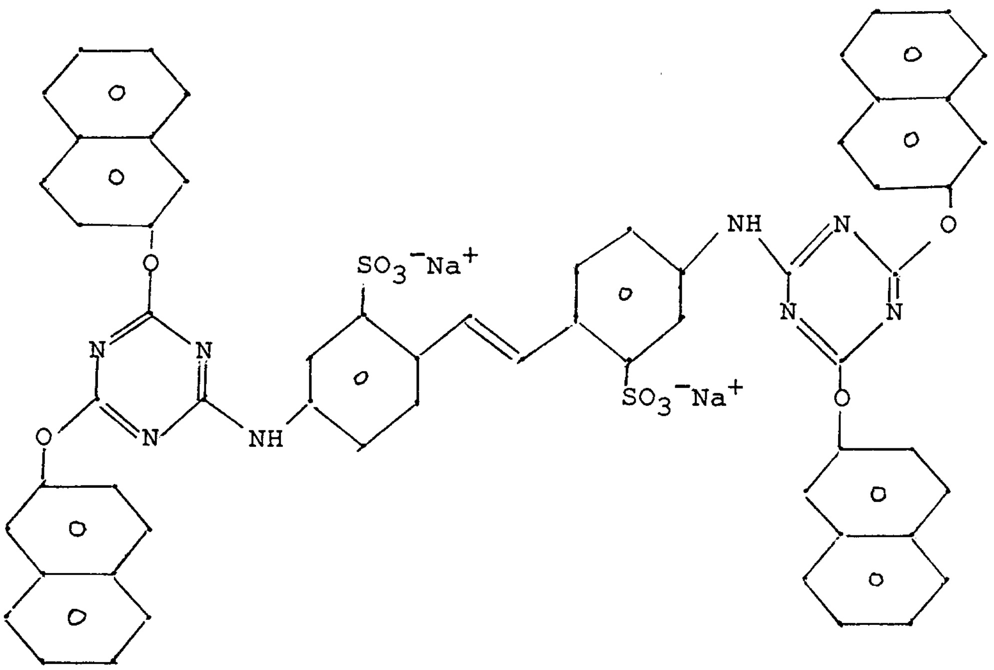
- evaluation in a photographic material

A high contrast sulfur plus gold sensitized cubic silver halide emulsion, doped with rhodium and iridium, was prepared, having an average grain size of 0.30 micron, and containing 0.4 % iodide, 16 % bromide and 83.4 % chloride. To 1 kg of emulsion, containing 1.10 moles of silver halide, was added a conventional substituted tetraazaindene and a conventional substituted mercaptotetrazole as antifoggant agents. A small amount of hydroquinone was added as an anti-oxidant. Then the emulsion was sensitized to the near infrared by a suitable amount of following sensitizer (IRS-1):



IRS-1

Then a supersensitizer, according to following formula, was added in a suitable amount:



Finally the pH was adjusted to 5.0.

The emulsion was coated onto a subbed polyethylene terephthalate support at an amount of silver halide corresponding to 7.5 g Ag/m^2, expressed as $AgNO_3$, and at 3.38 g/m^2 of gelatin. The photosensitive layer was overcoated with a layer containing 1 g/m^2 of gelatin, a matting agent and formaldehyde as gelatin hardener. Surfactants were added to both layers as coating aids.

The dried photographic material was cut in four parts and each part was overcoated with a first backing layer of different composition. The coating solutions of these first backing layers contained 54 g of gelatin, suitable amounts of colloidal silica, of a conventional wetting agent, and of a conventional hardening agent, and following amounts of a 2,83 % solution of dye ID-2 and of a 10 % solution of PMCD (table 3a):

TABLE 3a

	ml sol. of ID-2	ml sol. of PMCD	
sample 1'	150	-	(control)
sample 2'	150	375	(invention)
sample 3'	100	-	(control)
sample 4'	100	375	(invention)

The first backing layer of the four samples was overcoated with a second backing layer identical to the one of example 2. Then the four photographic materials were developed for 30 min at 35 °C in a conventional Rapid Access developer, containing hydroquinone and Phenidone as developing agents, fixed in a conventional ammonium sulphate containing fixer, and finally dried. For the determination of the residual colour the processed materials (five identical strips on top of each other) were measured using the CIELAB-method (see Farbmessung Grundlagen der Farbmetrik und ihre Anwendungsbereiche in der Druckindustrie Band 4, Verlag Beruf + Shule in Itzehoe, Hasl Loos, 1989) . This means that the colour is given in two numbers : a and b. These two figures describe each colour in a so called colour space. The results (table 3b) should be interpreted as follows :

a more negative, is more green
a more positive, is more magenta
a close to zero : no residual stain
L is luminance

TABLE 3b

Sample No.	a	L
1' (control)	5.0	66.0
2' (invention)	2.0	73.5
3' (control)	7.1	66.1
4' (invention)	1.9	72.6

From table 3b it is clear that the samples according to the invention show a spectacular decrease in residual colour stain after processing.

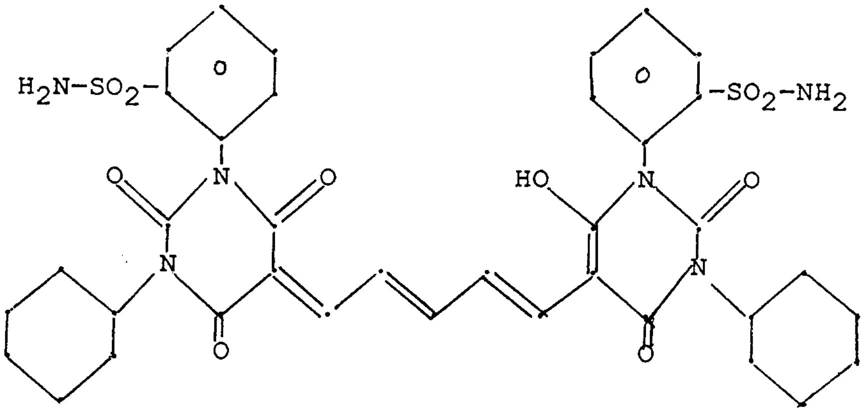
Claims

1. Photographic material comprising a support, at least one silver halide emulsion layer, and optionally one or more other hydrophilic layers, characterized in that at least one of said layers contains a cyclodextrin compound having a water-solubility of at least 10 g/100 ml, and a non-sensitizing dye capable of forming a clathrate with said cyclodextrin compound

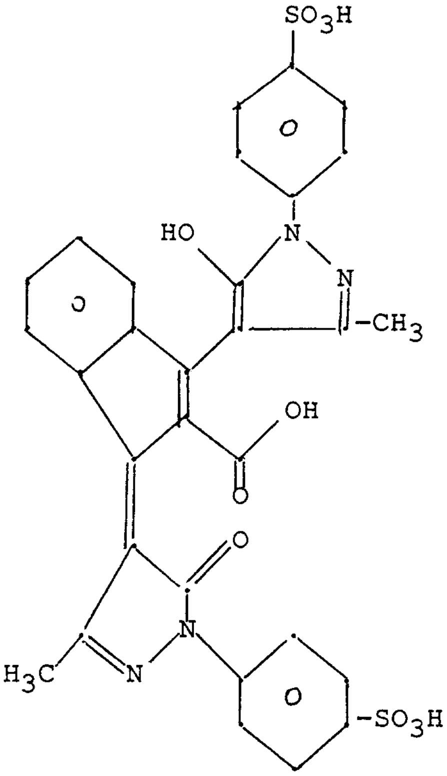
2. Photographic material according to claim 1 wherein said cyclodextrin compound is an etherified cyclodextrin derivative.

3. Photographic material according to claim 2 wherein said etherified cyclodextrin derivative is a partially methylated cyclodextrin.

4. Photographic material according to any of claims 1 to 3 wherein said non-sensitizing dye is following compound :



5. Photographic material according to any of claims 1 to 3 wherein said non-sensitizing dye is following compound :



Na

6. Photographic material according to claim 5 wherein said dye of claim 5 is incorporated in a backing layer, and said material is spectrally sensitized for the near infra-red.

7. Photographic material according to claim 6 wherein said infra-red sensitized material is an image-setting material.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0732

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.6)
X	DATABASE WPI Section PQ, Week 9415, Derwent Publications Ltd., London, GB; Class P83, AN 94-121466 & JP-A-667 347 (KONICA CORPORATION) 11 March 1994 * abstract *	1	G03C1/83 G03C1/835 G03C1/04
Y		2,3	

Y	DATABASE WPI Section PQ, Week 8743, Derwent Publications Ltd., London, GB; Class P83, AN 87-304220 & JP-A-62 215 261 (FUJI PHOTO FILM CO. LTD.) 21 September 1987 * abstract *	2,3	

A	FR-A-2 309 601 (AGFA-GEVAERT NV) *page 7,compound 7* * example 1 *	4	
	---		**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
A	DE-A-27 14 400 (FUJI PHOTO FILM CO. LTD.) * claim 1 *	5	G03C

D,A	EP-A-0 554 000 (KONICA CORPORATION) * page 23, line 10 - line 22 *	3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 September 1994	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document