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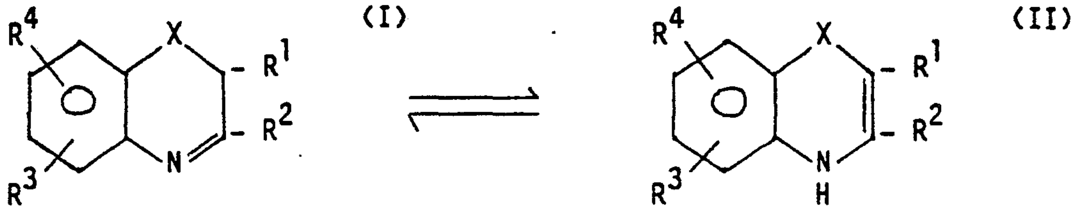
(54) Photographic element comprising benzoxazine or benzothiazine derivatives.

(57) Photographic element comprising on a support at least one silver halide emulsion layer and a speed-increasing amount of dispersed benzoxazine or benzothiazine derivative corresponding to general formula I or II:



wherein X is -O- or -S-, R^1 is hydrogen, alkyl, aryl, heterocyclyl, acyl, heterocyclylcarbonyl, alkyl- or aryl-carbamoyl, heterocyclylcarbamoyl, alkyl- or aryl-oxycarbonyl, or carboxy, R^2 is hydrogen, alkyl, alkyloxy, aryl, heterocyclyl, or hydroxy, and R^1 and R^2 together can represent a group of atoms completing a nucleus, and each of R^3 and R^4 (same or different) is hydrogen, halogen, alkyl, alkyloxy, aralkyloxy, aryl, alkenyl, acylamido, alkylamino, hydroxy, alkyl- or aryl-oxycarbonyl, alkyl- or aryl-oxycarbonyloxy, alkyl- or aryl-thio, or benzenesulphonyl.

PHOTOGRAPHIC ELEMENT COMPRISING BENZOXAZINE OR BENZOTHIAZINE DERIVATIVES

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a photographic element comprising a support and at least one silver halide emulsion layer comprising benzoxazine or benzothiazine derivatives as compounds increasing the sensitivity of the silver halide emulsion, hereinafter called speed-increasing compounds or derivatives.

2. Description of the Prior art:

It is known to increase the sensitivity of photographic silver halide emulsions by addition thereto of chemical sensitizers e.g. sulphur-containing compounds, reducing agents and salts of gold or other noble metals or combinations of these compounds. Such chemical sensitizers are believed to enter into reaction with the silver halide so as to form at the surface of the silver halide grains minute amounts of silver sulphide or of silver or of other noble metals, which increase the sensitivity of the silver halide emulsion. This kind of chemical sensitization, however, reaches a limit beyond which further addition of sensitizer or further digestion with the sensitizer merely induces an increase in fog of the emulsion whilst unaltering its speed or even lowering it.

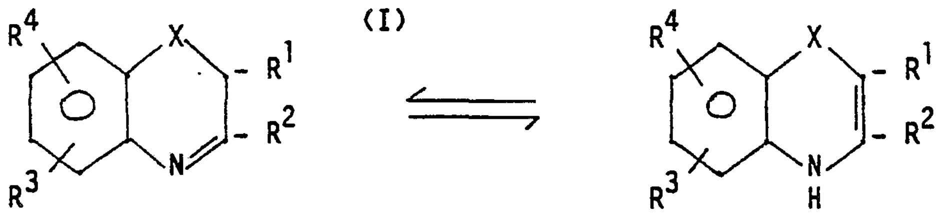
Another way of further increasing the sensitivity of photographic silver halide emulsions is by effecting the development in the presence of alkylene oxide polymers e.g. polyoxyethylene compounds, thioether compounds and/or onium or polyonium compounds of the ammonium, phosphonium, or sulphonium type. These classes of compounds sensitize the emulsion by development acceleration and can be used either in the emulsion or the developer. For instance in US-A 4,038,075 a method has been described for developing an imagewise exposed photographic silver halide emulsion with a developing solution containing derivatives of polyethylene glycol having at one or both sides a terminal group containing a thioether linkage. The problem with many of these classes of compounds is that while they increase the sensitivity they often tend to raise the fog level of silver halide emulsions. It is known in this respect from US-A 4,463,088 to use certain quinoxaline derivatives as antifogging agents for silver halide emulsions.

Still there remains a need to enhance the sensitivity of silver halide.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a photographic element comprising a silver halide emulsion layer incorporating compounds that improve the developability of the silver halide when exposed and that as a result of said improved developability act as speed-increasing compounds.

This and other objects are achieved by providing a photographic element comprising a support and coated thereon at least one silver halide emulsion layer, said emulsion layer or a non-photosensitive hydrophilic colloid layer in water-permeable relationship therewith comprising at least one dispersed compound in amounts increasing the sensitivity of the silver halide emulsion, characterized in that said at least one compound is chosen from the group of benzoxazine and benzothiazine derivatives corresponding to one of the following tautomeric general formulae I and II:


(I) (II)

wherein:

X represents an oxygen or sulphur atom,

R^1 is a substituent selected from the group consisting of hydrogen, a branched or unbranched alkyl group e.g. methyl, butyl, and tetradecyl, a substituted alkyl group e.g. carboxymethyl, an aryl group, a substituted aryl group, a heterocyclyl group, an acyl group e.g. acetyl, valeryl and benzoyl, a substituted acyl group e.g. 2-bromoacetyl and p-hexadecyloxy-benzoyl, a heterocyclylcarbonyl group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group e.g. N-[4-(2,4-di-tert.pentylphenoxy)-butyl]-carbamoyl, an arylcarbamoyl group, a substituted arylcarbamoyl group e.g. 2,4- or 2,5-dimethoxy-anilido and 2- or 4-methoxy-anilido, a heterocyclylcarbamoyl group, an alkyloxycarbonyl group e.g. methoxycarbonyl and ethoxycarbonyl, an aryloxycarbonyl group, and carboxy, and

R^2 is a substituent selected from the group consisting of hydrogen, a branched or unbranched alkyl group e.g. methyl, butyl, tetradecyl, and pentadecyl, a substituted alkyl group, an alkyloxy group e.g. hexadecyloxy, an aryl group e.g. phenyl, a substituted aryl group e.g. p-ethoxycarbonyloxy-phenyl, p-methoxy-phenyl, p-hydroxy-phenyl, 2,4-dimethoxy-phenyl, p-hexadecyloxy-phenyl, and 2,4-dimethoxy-5-bromo-phenyl, a heterocyclyl group, hydroxy, and

R^1 and R^2 together can represent a group of atoms e.g. $-(CH_2)4-$ and $-CO-CH_2-C(CH_3)_2-CH_2-$ completing a nucleus, and

each of R^3 and R^4 (same or different)

is a substituent selected from the group consisting of hydrogen, a halogen atom, a branched or unbranched alkyl group e.g. methyl and 1,1,3,3-tetramethylbutyl, a branched or unbranched alkyloxy group e.g. methoxy, an aralkyloxy group e.g. benzyloxy, an aryl group, an alkenyl group, an acylamido group, an alkylamino group, a hydroxy group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkyloxycarbonyloxy group, an aryloxycarbonyloxy group, an alkylthio group, an arylthio group, and a benzenesulphonyl group.

Thanks to the presence in the photographic element of the dispersed benzoxazine or benzothiazine compounds the developability of the silver halide upon exposure is improved substantially and the speed of the photographic element is increased. This increase in speed is not attended with a significant enhancement of the fog value.

DETAILED DESCRIPTION OF THE INVENTION

The speed-increasing benzoxazine and benzothiazine derivatives for use according to the present invention can be incorporated successfully into a hydrophilic colloid layer by dissolving them first in at least one water-immiscible oil-type solvent or oil-former, adding the resulting solution to an aqueous phase containing a hydrophilic colloid e.g. gelatin and a dispersing agent e.g. the sodium salt of dodecylbenzenesulphonic acid and the sodium salt of N-oleyl-N-methyltauride, passing the resulting mixture through a homogenizing apparatus so that a dispersion of the oily solution of the speed-increasing derivative in an aqueous medium is formed, mixing the dispersion with a hydrophilic colloid composition e.g. a gelatin silver halide emulsion, and coating the resulting composition in the usual manner to produce a system in which particles of speed-increasing benzoxazine and benzothiazine derivative, surrounded by an oily membrane, are distributed throughout the gel matrix. The dissolution of the benzoxazine and benzothiazine derivative in the oil-former may be facilitated by the use of an auxiliary low-boiling water-immiscible solvent, which is removed afterwards by evaporation.

The speed-increasing benzoxazine and benzothiazine derivatives are generally added in amounts ranging from 0.005 g to 15 g, preferably 0.25 g to 8.0 g, per 1.5 mol of silver halide.

The speed-increasing benzoxazine and benzothiazine derivatives for use according to the present invention can be dispersed in hydrophilic colloid compositions preferably with the aid of at least one known oil-former such as an alkyl ester of phthalic acid, preferably di-n-butyl phthalate, or a phosphoric acid ester, preferably tricresyl phosphate, or any of the oil-formers listed in EP-A 0,176,628, EP-A 0,084,692, and EP-A 86-202066.6.

For dispersing the speed-increasing benzoxazine and benzothiazine derivatives of the present invention the oil-formers can be used in widely varying concentrations e.g. in amounts ranging from about 0.1 to about 10 parts by weight and preferably from about 0.5 to about 2 parts by weight relative to the amount of the speed-increasing benzoxazine and benzothiazine derivatives dispersed therewith. Excellent results were accomplished with equal weights of oil-former and speed-increasing compound.

It may be useful to combine at least one of the above defined oil- formers with at least one auxiliary solvent that is insoluble or almost insoluble in water and has a boiling point of at most 150 °C, such as lower alkyl acetates e.g. ethyl acetate or any of the auxiliary solvents mentioned in EP-A 0,176,628. The auxiliary solvent may also be a water-soluble organic solvent such as methanol, ethanol, isopropanol, dimethylsulphoxide, tetrahydrofuran, N-methylpyrrolidone, dioxan, acetone, butyrolactone, ethylene glycol, ethylene glycol monomethyl ether, ethy lene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether, glycerol, acetonitrile, formamide, dimethylformamide, tetrahydrothiophene dioxide, or dimethoxyethane. The auxiliary solvent may also be one described in i.a. US-A 2,801,170; 2,801,171; 2,949,360; 2,835,579.

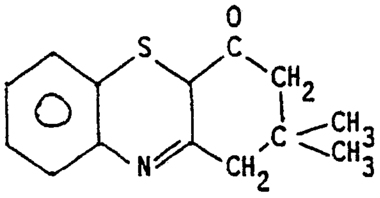
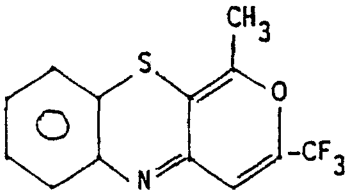
Representatives of said benzoxazine and benzothiazine derivatives corresponding to one of the tautomeric general formulae I and II that can be used in accordance with the present invention are listed in the following Table 1.

TABLE 1:

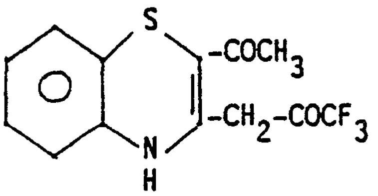
a) Benzoxazine derivatives:

Compound N°		melting at (°C)
1	3-p-hexadecyloxyphenyl-benzoxazine (A,B)	102
2	3-p-hexadecyloxyphenyl-6-benzenesulphonyl-benzoxazine (A)	89
3	2-[2-chloro-5-(2,4-di-tert.pentylphenyloxy)-butyramido]-anilido-3-tert.butyl-benzoxazine (A,B)	147
4	2-[2-chloro-5-(2,4-di-tert.pentylphenyloxy)-butyramido]-anilido-3-tert.butyl-6-methyl-benzoxazine (B)	151
5	2-(2,5-dimethoxy-4-N-hexadexylsulphamoyl)-anilido-3-tert.butyl-benzoxazine (B)	90
6	2-tetradecyl-3-p-methoxyphenyl-benzoxazine (B)	62
7	2-(2,4-dimethoxy)anilido-3-tert.butyl-6-(1,1,3,3-tetramethyl)butyl-benzoxazine (B)	127
8	2-butyl-3-p-methoxyphenyl-benzoxazine (B)	oil
9	2-[2-chloro-5-(2,4-di-tert.pentylphenyloxy)-butyramido]-anilido-3-tert.butyl-6-methoxy-benzoxazine (B)	159-160
10	3-hexadecyloxy-6-methoxy-benzoxazine (B)	71
11	3-phenyl-benzoxazine (B)	113
12	2-(2,4-dimethoxy)anilido-3-tert.butyl-benzoxazine (B)	137
13	2-N-[4-(2,4-di-tert.pentylphenoxy)-butyl]-carbamoyl-3-tert.butyl-benzoxazine (B)	110

b) Benzothiazine derivatives:

Compound N°		melting at (°C)
14	3-p-hexadecyloxyphenyl-benzothiazine (C)	78.5
15	2-ethoxycarbonyl-3-tert.butyl-benzothiazine (C)	oil
16	2-ethoxycarbonyl-3-methyl-benzothiazine (D)	145
17	2-acetyl-3-methyl-benzothiazine (D)	144
18	2-[2-chloro-5-(2,4-di-tert.pentylphenyloxy)-butyramido]-anilido-3-tert.butyl-benzothiazine (C)	155-157
19	2-butyl-3-p-methoxyphenyl-benzothiazine (C)	oil
20	2-butyl-3-(2,4-dimethoxy-5-bromo)phenyl-benzothiazine (C)	130
21	3-p-ethoxycarbonyloxy-phenyl-benzothiazine (C)	96
22	3-p-hydroxyphenyl-benzothiazine	132
23	2-methyl-3-p-hydroxyphenyl-benzothiazine	155
24	2-methoxycarbonyl-3-pentadecyl-benzothiazine	88
25	2-(2,4-dimethoxy)anilido-3-tert.butyl-benzothiazine	115-116
26	2-o-methoxyanilido-3-methyl-benzothiazine (D)	145-158
27	2-(2,5-dimethoxy)anilido-3-p-hexadecyloxyphenyl-benzothiazine (C)	94
28	2-valeryl-3-hydroxy-benzothiazine (D)	149.5
29	2-benzoyl-3-hydroxy-benzothiazine (D)	189.5
30	2-carboxymethyl-3-hydroxy-benzothiazine	188
31	compound according to the following structural formula: 	273
32	compound according to the following structural formula: 	149

33 compound according to the following structural formula: 132



The benzoxazine speed-increasing compounds according to the present invention can be prepared by reductive cyclization of 2-nitrophenoxyaceto compounds (method A) or by cyclocondensation of 2-aminophenols with Alpha-halogen-keto compounds (method B).

The benzothiazine speed-increasing compounds according to the present invention can be prepared by cyclocondensation of 2-aminothiophenols with Alpha-halogen-keto compounds (method C) or by oxidative cyclization of Beta-diketo compounds with o-aminothiophenols in dimethylsulphoxide (method D).

In Table 1 the method or, as the case may be, the methods according to which the identified compounds have been synthesized is (are) indicated between parentheses after the name of said compound.

According to these methods A to D the compounds for use according to the present invention can be prepared very simply and very economically.

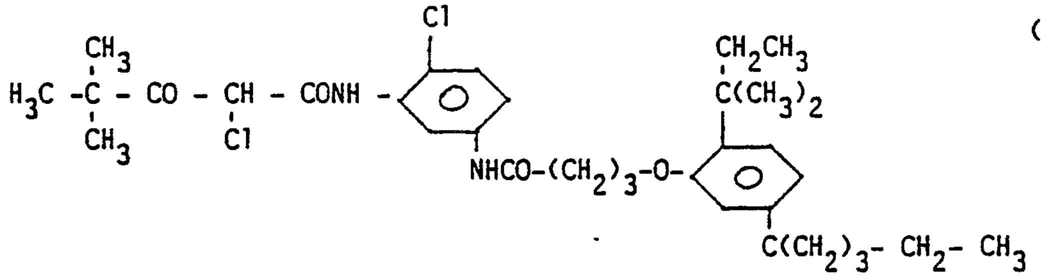
A description of the synthesis of some of the compounds identified in Table 1 is given hereinafter by way of example. The synthesis of other compounds identified in Table 1 as well as of compounds not identified in Table 1 but corresponding to the above general formulae I and II can easily be derived from the preparation examples described hereinafter.

Preparation 1 according to Method A : Compound 2

A mixture of 88 g (0.2 mol) of 1-Omega-bromoacetyl-4-n-hexadecyloxy- benzene, 56 g (0.2 mol) of 5-benzenesulphonyl-2-nitro-phenol, and 27.6 g (0.2 mol) of potassium carbonate and 500 ml of dimethylformamide is heated for 2 h at 50° C and then poured out in water. The yellow grainy precipitate is filtered off, dried, and recrystallized from acetone. In an autoclave an amount of 31.85 g of the resulting precipitate is reduced catalytically with Raney-nickel in 200 ml of dimethylformamide under an initial hydrogen pressure of 10500 kPa at a temperature of 65° C. The reaction time is 3 h. Next, the catalyst is filtered off and the resulting filtrate is cooled in a deep-freezer.
Yield: 19.5 g of Compound 2.

Preparation 2 according to Method B : Compound 3

A mixture of 30.3 g (0.05 mol) of the Alpha-halogen-keto compound AHK according to the following structural formula:



(AHK)

5.7 g (0.055 mol) of o-aminophenol, 12.5 ml of tetramethylguanidine, and 100 ml of acetonitrile is stirred for 3 h at room temperature. Next, 300 ml of 2N hydrochloric acid was added. An oil is formed, which solidifies overnight. The precipitate is dried and purified by column chromatography.
Yield: 17 g of Compound 3.

Preparation 3 according to Method D : Compound 17

A mixture of 27.5 g (0.2 mol) of o-aminothiophenol, 20 g (0.2 mol) of 2,4-pentanedione, and 100 ml of dimethyl sulphoxide is heated for 20 min at 130 °C whilst distilling off the dimethylsulphide formed. The mixture is poured out in water. The precipitate is filtered, dried, and purified by column chromatography.
Yield: 23.3 g of Compound 17.

Preparation 4 according to Method C : Compound 18

A mixture of 30.25 g (0.05 mol) of the above described compound AHK, 6.25 g (0.05 mol) of o-aminothiophenol, and 220 ml of acetonitrile is heated for 15 min at 80 °C. Upon cooling a yellow precipitate is formed and filtered off. The filtrate is stirred twice in 250 ml of water, filtered off, dried, and crystallized from ethanol.
Yield: 24 g of white Compound 18.

Preparation 5 according to Method C : Compound 21

a) A volume of 19.7 ml (0.2 mol) of ethyl chloroformate is added in 30 min to a solution of 27 g (0.2 mol) of 4-hydroxy-acetophenone in a mixture of 150 ml of acetonitrile and 20 ml of pyridine. The reaction mixture is stirred for 30 min and poured out in hydrochloric acid. The precipitate is filtered off.
Yield: 36.5 g of intermediate compound (a).

b) An amount of 36.5 g (0.175 mol) of intermediate compound (a) is dissolved in 230 ml of methylene chloride. The solution obtained is cooled to 10 °C and a solution of 9 ml of bromine in 20 ml of methylene chloride is added dropwise thereto in 30 min. After 1 h of stirring 25 ml of ethanol is added and the whole is concentrated until dry.
Yield: 50 g (100%) of green oily intermediate product (b).

c) An amount of 21.9 g (0.175 mol) of o-aminothiophenol is added to a solution of 48.8 g (0.175 mol) of intermediate product (b). The mixture is heated at 50 °C for 4 h and cooled. The yellow precipitate is filtered off, stirred in a 10% aqueous solution of sodium hydrogen carbonate, neutralized with acetic acid, and filtered off. The filtrate is dried and recrystallized from acetonitrile.
Yield: 27 g of Compound 21.

Preparation 6 : Compound 22

An amount of 18.8 g (0.06 mol) of Compound 21 is suspended in a mixture of 50 ml of ethanol, 100 ml of water, and 1 g of sodium dithionite. A volume of 25 ml of 5N sodium hydroxide is added to the suspension. The whole is heated to 50 °C. After 30 min a yellow solution is obtained, which is diluted with 200 ml of ice-water and neutralized with acetic acid. The yellow precipitate formed is filtered off and crystallized from acetonitrile.
Yield: 11.1 g of Compound 22.

The speed-increasing benzoxazine and benzothiazine derivatives used in accordance with the present invention can be incorporated into any type of photographic element comprising a light-sensitive silver halide emulsion layer e.g. a spectrally sensitized silver halide emulsion layer, a non-spectrally sensitized silver halide emulsion layer, a silver halide emulsion layer of use in diffusion transfer reversal processes for the production of silver images, an X-ray silver halide emulsion layer, a silver halide emulsion layer for use in graphic arts e.g. a lith silver halide emulsion layer, a silver halide emulsion layer sensitive to infra-red radiation, a silver halide emulsion layer used in a photographic element for so-called amateur or professional photography, in low-speed or high-speed photographic elements.

The halide composition of the silver halide emulsions used according to the present invention is not specifically limited and may be any composition selected from i.a. silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide.

The photographic silver halide emulsions used according to the present invention 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 silver halide particles of the photographic emulsions used according to the present invention 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 inbetween.

Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in accordance with the present invention.

The average size of the silver halide grains may range from 0.2 to 0.7 µm, preferably from 0.4 to 0.5 µm.

The size distribution of the silver halide particles of the photographic emulsions to be used according to the present invention 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.

In addition to silver halide the emulsions may also comprise organic silver salts such as e.g. silver benzotriazolate and silver behenate.

The silver halide crystals can be doped with Rh^{3+}, Ir^{4+}, Cd^{2+}, Zn^{2+}, Pb^{2+}.

The photographic emulsions can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966). They can also be prepared as described in the paper entitled "Halide compositional and distributional analysis of iodide-converted silver bromide microcrystals by secondary ion mass spectrometry and scanning transmission electron microscopy with energy-dispersive X-ray detection" by Gao Xiu-lin, J. van Vooren, R. Gijbels, Y. Gilliams, and M. Kelchtermans in the "Proceedings of the International Congress of Photographic Science" Cologne, 1986, published by Fr. Granzer en E. Moisar; editor Friedr. Vieweg & Sohn, Braunschweig/Wiesbaden, Federal Republic of Germany. According to this paper iodide-converted silver bromoiodide emulsions comprising 5 mol% of silver iodide are prepared. It is, however, possible according to this method of emulsion preparation to increase the iodide content to as high as 15 mol% of silver iodide calculated on the total amount of silver halide.

The emulsions can be desalted in the usual ways e.g. by dialysis, by flocculation and re-dispersing, or by ultrafiltration.

Besides the silver halide another essential component of a light-sensitive emulsion layer is the binder. The binder is a hydrophilic colloid, preferably gelatin. Gelatin can, however, be replaced in part or integrally by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, 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 of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates.

The binder should dispose of an acceptably high number of functional groups, which by reaction with an appropriate hardening agent can provide a sufficiently resistant layer. Such functional groups are especially the amino groups, but also carboxylic groups, hydroxy groups, and active methylene groups.

The 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 light-sensitive silver halide emulsion can be a so-called primitive emulsion, in other words an emulsion that has not been chemically sensitized. However, the light-sensitive silver halide emulsion can be chemically sensitized as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "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-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used.

The light-sensitive silver halide emulsions can be 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, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A 2,933,390 and US-A 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510, cadmium salts, and azaindene compounds.

The silver halide emulsion for use in accordance with the present invention 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, 1-phenyl-Delta-2-tetrazoline-5-thione, oxazolinethione, 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-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, 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), Chaptre 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.

The binders of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone 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.

The photographic element of the present invention 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 alkylaryl 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, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, 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.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805 - 4,038,075 - 4,292,400.

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

According to certain photographic rapid access systems the photographic element is a cadmium-free highly sensitive orthochromatic silver halide element comprising developing agents in the light-sensitive hydrophilic colloid silver halide emulsion layer or in an adjacent hydrophilic colloid layer in water-permeable relationship therewith e.g. in a subbing layer or adhesive layer. According to such rapid access systems the exposed photographic element is developed by processing it merely with an alkaline activating liquid. Development can then be followed by stabilization as described in e.g. US-A 4,030,924. In these rapid access systems it may be advantageous to partially replace the hydrophilic colloid binder, preferably gelatin, of the light-sensitive silver halide emulsion layer or of an adjacent hydrophilic colloid layer in water-permeable relationship therewith, by suitable amounts of dextran or dextran derivatives. It has been experienced indeed that by adjusting a weight ratio of 2 to 13 parts of dextran or derivatives thereof per 10 parts of gelatin in the silver halide emulsion layer or in the adjacent subbing layer the covering power of the silver image formed in the developed photographic element can be enhanced substantially. This enhanced covering power can also be profitable in that less silver coverage is needed in the preparation of the silver halide emulsion. The use of dextran or derivatives thereof in the photographic element also offers the advantage that a higher resistance to abrasion in wet condition before and after development can be obtained. Furthermore, the stability during storage of the photographic element comprising dextran or derivatives thereof is improved substantially.

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, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

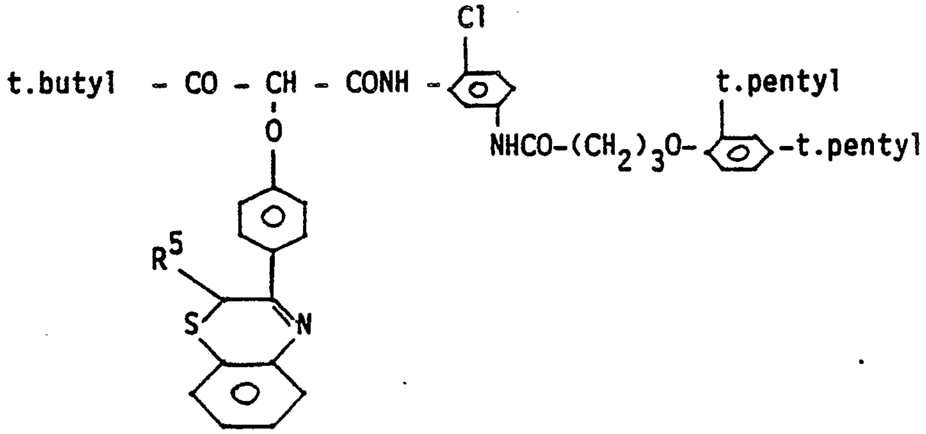
Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 µm. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US-A 4,614,708.

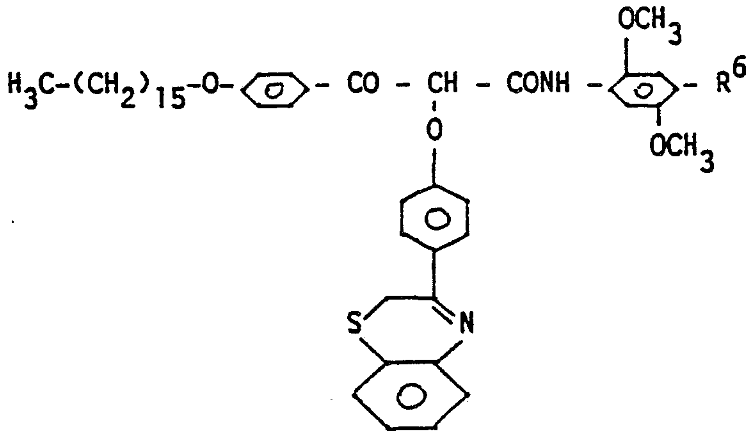
It has also been established that the benzoxazine and benzothiazine structures according to the general formulae I and II can be used advantageously in colour photographic silver halide elements as coupling off groups that constitute an integral part of colour couplers incorporated therein, which colour couplers during reaction with an oxidized primary amino developing agent form a coloured image dye e.g. a cyan, magenta, or yellow image dye and at the same time release the speed-increasing benzoxazine or benzothiazine moiety.

Suitable representatives of such couplers are the following, the method or, as the case may be, the methods described hereinafter according to which the identified compounds can be synthesized being indicated between parentheses:

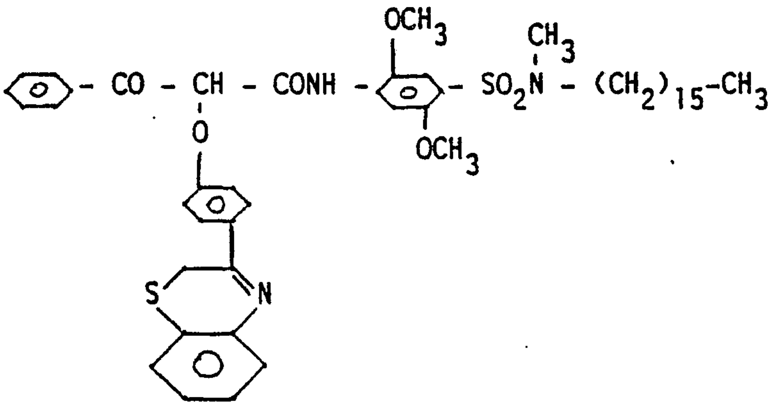
Yellow-forming couplers according to the following formula:



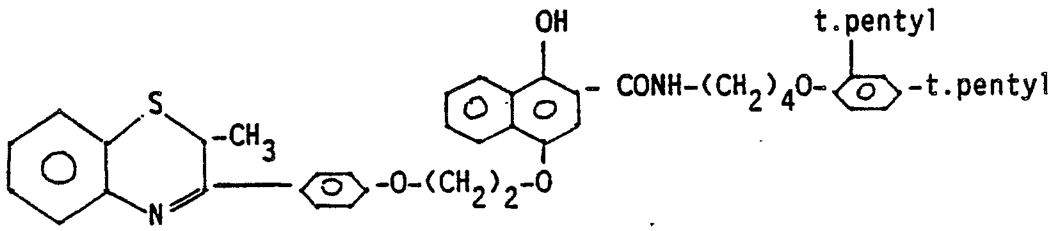
Coupler Y01 , R^5 representing methyl (method E) melting at 94-96° C
Coupler Y02 , R^5 representing hydrogen (method E) melting at 80-90° C
Yellow-forming couplers according to the following formula:



Coupler Y03 , R^6 representing bromo (method F) melting at 85° C
Coupler Y04 , R^6 representing chloro (method E or F) melting at 90-97° C
Coupler Y05 , R^6 representing hydrogen (method F) melting at 85° C
Coupler Y06 according to the following formula: (method F) (melting 168° C)



Cyan-forming Coupler C01 according to the following formula: (melting at 153° C:

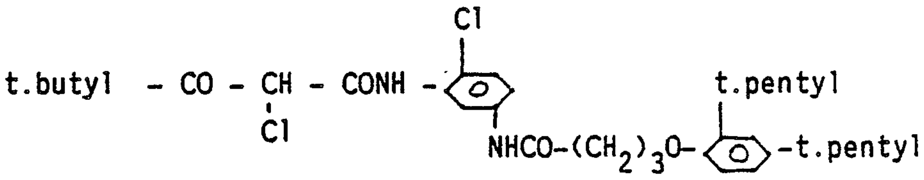


The above colour couplers can be prepared by synthesizing the benzoxazine or benzothiazine moiety and then making it react with a colour coupler that has been chlorinated first at the coupling off position (method E).

A description of the synthesis of Coupler Y02 according to this method is given hereinafter by way of example.

Preparation of Coupler Y02 according to Method E

An amount of 12.1 g (0.02 mol) of yellow-forming coupler according to the following formula:

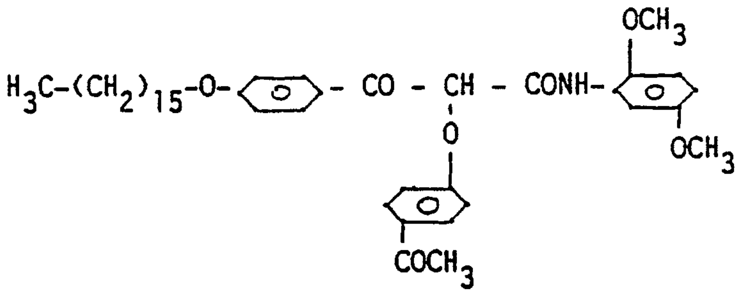


4.82 g (0.02 mol) of Compound 22 prepared as described above, 80 ml of acetonitrile, and 5 ml (0.04 mol) of tetramethylguanidine are placed in reaction flask. The temperature rises to 36 °C. After 15 min of stirring a precipitate settles. Stirring is continued for 2 h. The yellow precipitate is filtered with suction and dissolved with methylene chloride. The resulting solution is mixed with aqueous acetic acid. After separation the solvent is removed by evaporation. The residue is purified by column chromatography on silanated silica.
Yield: 8.2 g of Coupler Y02. Melting range: 80-90 °C.

It is also possible to prepare the colour couplers according to the following method F.

Preparation of Coupler Y05 according to Method F

A solution of 10.3 ml (0.2 mol) of bromine in 400 ml of methylene chloride is added in 90 min to a chilled solution (0 °C) of 67.3 g (0.1 mol) of compound according to the following formula:

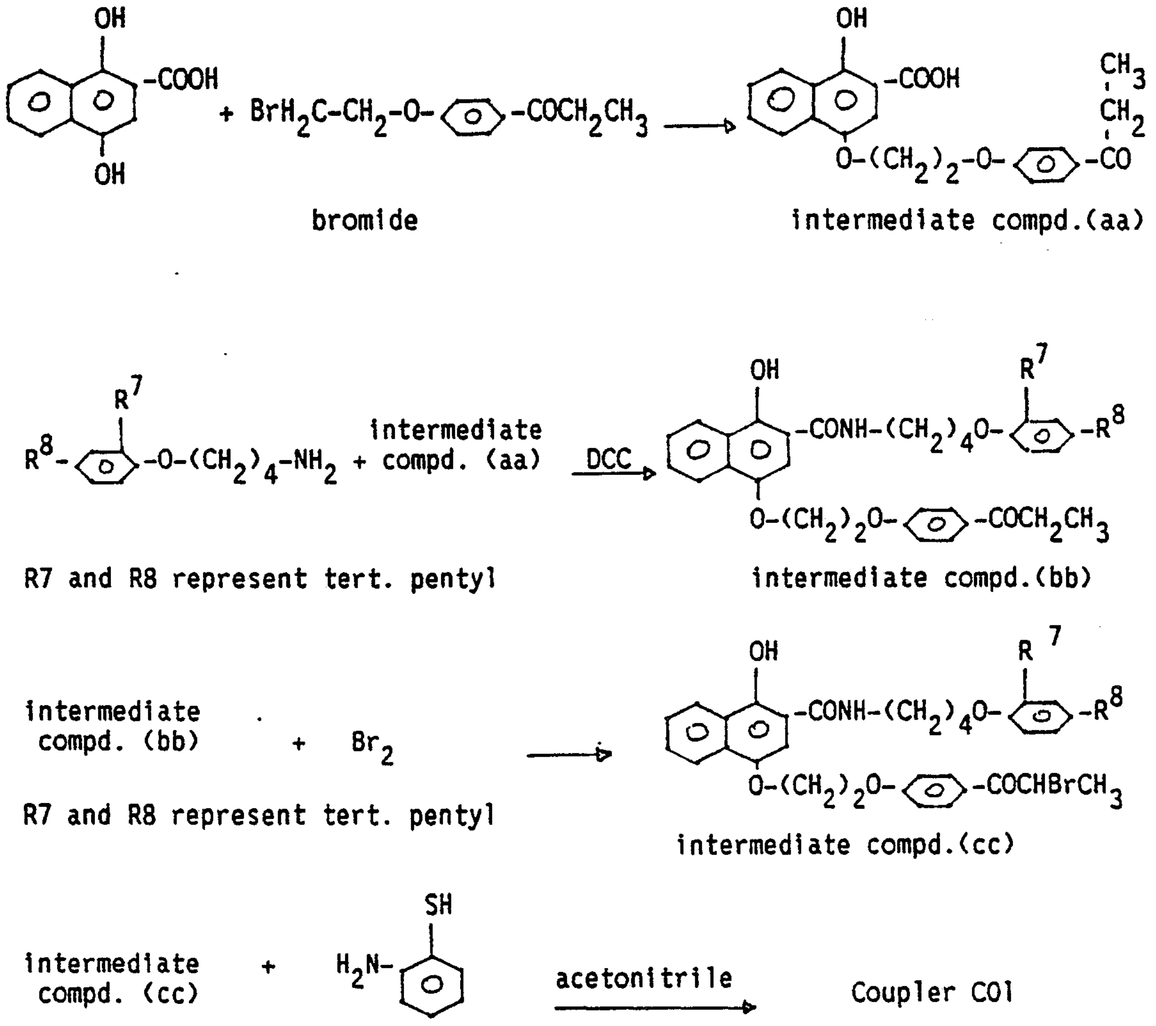


The reaction mixture is stirred for 2 h. A volume of 80 ml of methanol is added. The whole is concentrated by evaporation. The oil obtained is stirred with 200 ml of ethyl acetate and the resulting precipitate is filtered off and recrystallized from ethyl acetate.
Yield: 38 g . Melting point 84 °C.

A mixture of 7.5 g (0.01 mol) of this product and 1.5 g (0.012 mol) of o-aminothiophenol in 100 ml of acetonitrile is heated for 2 h at 50-55° C. After cooling the resulting precipitate is filtered off. The precipitate is stirred for 10 min in a mixture of 100 ml of ethanol and 20 ml of saturated aqueous solution of sodium carbonate. After neutralization with acetic acid the precipitate is separated, dried, and recrystallized from ethyl acetate.

Yield: 2.3 g (30%). Melting point: 85° C.

It is also possible to prepare the colour couplers according to the following reaction scheme, in which the synthesis of Coupler C01 is represented :



Step 1 : A solution of 61.2 g (0.3 mol) of dihydroxynaphthoic acid in 300 ml of dimethylformamide is added dropwise to a suspension of 28.8 g (0.6 mol) of sodium hydride in 450 ml of dimethylformamide. The mixture is stirred for 1 h and then chilled to 5° C. A solution of 77.1 g (0.3 mol) of the above bromide in 250 ml of dimethylformamide is added in 30 min, while the temperature is maintained under 10° C. Next, the reaction mixture is stirred at room temperature for 4 h. A volume of 120 ml of 5N hydrochloric acid is added together with 1 l of demineralized water. The resulting precipitate is filtered, dried, and boiled up with acetonitrile.

Yield: 77 g of the intermediate product (aa) melting at 207° C.

Step 2 : A solution of 38 g (0.1 mol) of the intermediate product (aa), 30.5 g (0.1 mol) of the amino compound represented in the above reaction scheme , and 22.7 g (0.11 mol) of dicyclohexyl carbodiimide (DCC) in methylene chloride is stirred for 24 h at room temperature. The precipitate (dicyclohexyl urea) is filtered with suction and the filtrate is concentrated by evaporation. The residue is purified by column chromatography.

Yield: 34 g of the intermediate product (bb) melting at 85° C.

Step 3 : A solution of 3.2 g (0.02 mol) of bromine in 30 ml of methylene chloride is added to a solution of

13.34 g (0.02 mol) of the intermediate product (bb) in 30 min at approximately 10 °C. The mixture is stirred for 2 h at room temperature and added to a 10% aqueous sodium hydrogen carbonate solution. The methylene chloride is removed by evaporation and the residue is concentrated by evaporation and purified by column chromatography.
Yield: 6 g of the intermediate product (cc) melting at 50-55 °C.
Step 4 : A mixture of 5.22 g (0.007 mol) of the intermediate product (cc), 0.875 g of o-aminothiophenol and 40 ml of acetonitrile is first stirred for 6 h at room temperature and next for 15 min at 75 °C. A volume of 50 ml of hot water is added to the orange mixture. A tacky precipitate settles and converts into a grainy product upon cooling. The product is filtered and extracted with methylene chloride. The residue is concentrated by evaporation and purified by column chromatography.
Yield: 1.7 g of Coupler C01 melting at 153 °C.

The following examples illustrate the present invention.

EXAMPLE 1

Preparation of a dispersion of speed-increasing compound according to the present invention

A volume of 100 ml of 5% aqueous gelatin is mixed with 5 to 10% of sodium salt of dodedylbenzenesulphonic acid (calculated on the weight of the gelatin) as dispersing agent. The resulting mixture is dispersed at 40 °C. A solution of 1 g of speed-increasing benzoxazine or benzothiazine derivative according to the present invention and 1 g of dibutyl phthalate in 5 ml of ethyl acetate is added in 30 s with stirring to the dispersion. The ethyl acetate is removed by heating the mixture to 60 °C in a rotating thin-layer evaporator at about 5 kPa.

Preparation of photographic element according to the present invention

An amount of 210 g of a silver bromoiodide emulsion (3.5 mol% of iodide) having a gelatin content of 120 g per kg and a silver halide content corresponding to 190 g of silver nitrate per kg was mixed in molten state with 100 g of dispersion of speed-increasing compound as identified in Table 2 hereinafter, the dispersion having been prepared as described above.

The emulsion was coated on both sides of a polyethylene-coated paper support at a ratio of 4.25 g per m2 per side. The coated emulsion layers were dried.

Preparation of photographic Comparison element

A photographic Comparison element was made in exactly the same way as described above for the photographic element according to the present invention, except for the fact that no dispersion of speed-increasing compound was added to the silver bromoiodide emulsion of the photographic Comparison element.

Exposure and Development

Two identical samples of each of the above described photographic elements were exposed in the same way to white light through a filter having a peak emission at 534 nm and a peak width at half height of 64 nm.

All exposed samples were developed at 34 °C in a processing machine comprising developer G 136 marketed by Agfa-Gevaert N.V., Mortsel, Belgium. For a first series consisting of one sample of each of the exposed above described photographic elements the total time elapsing between the moment of immersion in the developing bath and the moment of complete dryness again was set at 60 s, the actual development time being 12 s. For the second series of samples also consisting of one sample of each of the exposed above described photographic elements the total time between immersion and complete dryness was set at 120 s, the actual development time being 33 s.

The developability of the photographic elements was determined by measuring the speed at the two different development times (12 s and 33 s as specified above). The difference between both these speed values is a measure for the developability of the photographic elements.

Delta Speed = $\text{Speed}_{33} - \text{Speed}_{12}$

The smaller the difference , the better the developability.

If $(\text{Delta Speed})_0$ stands for the developability of the photographic Comparison element (expressed in DIN) and $(\text{Delta Speed})_1$ stands for the developability of the photographic element comprising a speed-increasing compound according to the present invention, the gain in developability is

$(\text{Delta Speed})_0 - (\text{Delta Speed})_1$ (expressed in DIN).

The gain in developability obtained with the photographic elements comprising the speed-increasing benzoxazine and benzothiazine derivatives according to the present invention is given in Table 2.

The values of fog are also given in Table 2.

TABLE 2

Speed-increasing Compound	Gain in Developability (expressed in DIN)	Fog
Comparison element	0.0	0.24
1	0.4	0.24
3	0.5	0.26
14	1.3	0.28
18	0.4	0.24
25	1.0	0.26

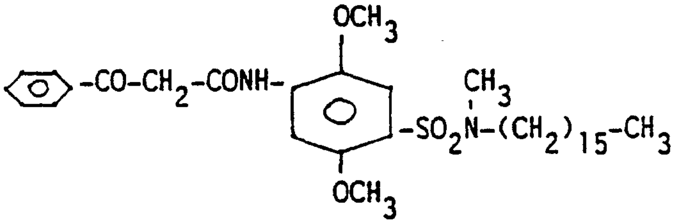
It is seen that not only the speed was favourably increased but also the fog level of the silver halide emulsion was not impaired significantly.

EXAMPLE 2

Preparation of Blank Element A

An amount of 114.6 g of blue-sensitive silver bromoiodide emulsion (2.3 mol% of iodide) comprising per kg an amount of 73.4 g of gelatin and an amount of silver halide equivalent to 47 g of silver nitrate was diluted with 127 ml of a 7.5 % by volume solution of gelatin in 100 ml of distilled water.

A dispersion of yellow-forming coupler was made by dissolving 0.006 mol of coupler corresponding to the following structural formula:



in 16 ml of ethyl acetate and 2 g of dibutyl phthalate, dispersing the resulting solution in 100 ml of a 5 % by volume aqueous solution of gelatin containing 0.4 g of the sodium salt of dodecylbenzene sulphonic acid by means of an ultrasonic power generator, and eliminating the ethyl acetate by evaporation under reduced pressure.

The resulting dispersion was added to the blue-sensitive emulsion.

After neutralization of the emulsion and addition thereto of the usual additives such as stabilizing agents, wetting agents, and hardening agents the necessary amount of water to obtain 575 g of emulsion was added.

The emulsion was coated on a film support at a ratio of 150 g per m2. The emulsion layer was dried and covered with a gelatin layer. The resulting element was used for comparison and is called Blank A hereinafter.

Preparation of colour photographic element according to the present invention

Colour photographic element A

A colour photographic element A was made in exactly the same way as described above for the Blank A, except for the fact that a dispersion (prepared as described in Example 1) of speed-increasing compound 15 of Table 1 was added to the silver bromoiodide emulsion in a ratio of 10 % by weight calculated on the weight of the yellow-forming coupler.

Exposure and Development

The Blank A and colour photographic Element A were exposed in a Herrnfeld sensitometer for 1/20 s through a continuous wedge with a constant of 0.30.

The exposed samples were colour processed in the usual way, which includes colour development, bleaching, and fixing. The developing agent was 4-amino-N-ethyl-N-(Beta-methanesulphonamidoethyl)-m-toluidine sesquisulphate monohydrate, the development time being 15 min and the temperature of development being 21 °C.

In Table 3 hereinafter the values measured for maximum density (Dmax), fog, and speed are given. The values given for speed are relative values, a value of 100 being given to the Blank Element A. A value of 200 would correspond to a doubling of the speed.

TABLE 3

	Dmax	Speed	Fog
Blank A	263	100	0.40
Colour photographic element A	267	112	0.40

Comparison of the results shows that the speed is enhanced substantially when the speed-increasing compound is present in the material and that this increase in speed is not attended with an enhancement of the fog value. It is also seen that the maximum density has improved as well.

EXAMPLE 3

Preparation of Blank Element B

An amount of 118.2 g of red-sensitized silver bromoiodide emulsion (10.0 mol% of iodide) comprising per kg an amount of 72.5 g of gelatin and an amount of silver halide equivalent to 145 g of silver nitrate was diluted with 38.8 ml of a 7.5 % by volume solution of gelatin in 100 ml of distilled water.

A dispersion of cyan-forming coupler was made by dissolving 0.0015 mol of the coupler disclosed as Colour coupler II in Example 3 of US-A 3,980,481, in 16 ml of ethyl acetate and 2 g of dibutyl phthalate, dispersing the resulting solution in 100 ml of a 5 % by volume aqueous solution of gelatin containing 0.4 g of the sodium salt of dodecylbenzene sulphonic acid by means of an ultrasonic power generator, and eliminating the ethyl acetate by evaporation under reduced pressure.

The resulting dispersion was added to the red-sensitized emulsion.

The usual additives were added and an emulsion layer was coated therefrom as described in Example 2. The dry emulsion layer was covered with a gelatin layer.

The resulting element was used for comparison and is called Blank B hereinafter.

Preparation of colour photographic element according to the present invention

Colour photographic element B

A colour photographic element B was made in exactly the same way as described above for the Blank B, except for the fact that a dispersion of speed-increasing compound 16 of Table 1, prepared as described in Example 1, was added to the silver bromoiodide emulsion in a ratio of 0.1 mol% of compound 16 in respect of the amount of cyan-forming coupler added.

Exposure and Development

The Blank B and the colour photographic Element B were exposed and colour processed as described in Example 2 hereinbefore.

In Table 4 hereinafter the values measured for maximum density (Dmax), fog, and speed are given. The values given for speed are relative values as defined in the foregoing Examples.

TABLE 4

	Dmax	Speed	Fog
Blank B	153	100	0.22
Colour photographic element B	197	120	0.24

Comparison of the results shows that the speed is enhanced substantially when the speed-increasing compound is present in the material and that this increase in speed is not attended with a significant enhancement of the fog value. It is also seen that the maximum density has improved as well.

EXAMPLE 4

Preparation of Blank Element C

The preparation of Blank Element C was fully identical to that of Blank Element B.

Preparation of colour photographic element according to the present invention

Colour photographic element C

A colour photographic element C was made in exactly the same way as described above for the Blank C, except for the fact that a dispersion (prepared as described in Example 1) of speed-increasing compound 13 of Table 1 was added to the silver bromoiodide emulsion in a ratio of 10 mol% of compound 13 in respect of the amount of cyan-forming coupler added.

Exposure and Development

The Blank C and the colour photographic Element C were exposed and processed as described in Example 2.

In Table 5 hereinafter the values measured for maximum density (Dmax), fog, and speed are given. The values given for speed are relative values as defined in the foregoing Example 2.

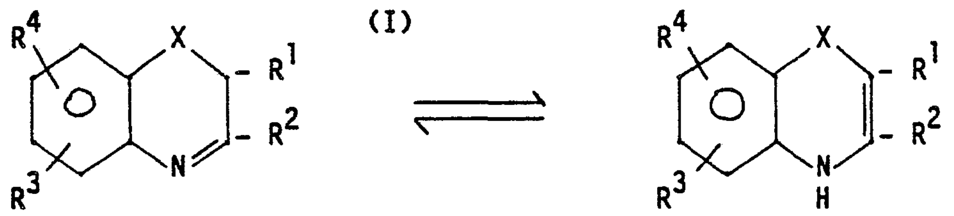
TABLE 5

	Dmax	Speed	Fog
Blank C	178	100	0.24
Colour photographic element C	180	110	0.25

Comparison of the results shows that the speed is enhanced when the speed-increasing compound is present in the material and that this increase in speed is not attended with a significant enhancement of the fog value. It is also seen that the maximum density has improved slightly.

Claims

1. Photographic element comprising a support and coated thereon at least one silver halide emulsion layer, said emulsion layer or a non-photosensitive hydrophilic colloid layer in water-permeable relationship therewith comprising at least one dispersed compound in amounts increasing the sensitivity of the silver halide emulsion, characterized in that said at least one compound is chosen from the group of benzoxazine and benzothiazine derivatives corresponding to one of the following tautomeric general formulae I and II:



(I) (II)

wherein:

X represents an oxygen or sulphur atom,

R^1 is a substituent selected from the group consisting of hydrogen, a branched or unbranched alkyl group, a substituted alkyl group, an aryl group, a substituted aryl group, a heterocyclyl group, an acyl group, a substituted acyl group, a heterocyclylcarbonyl group, an alkylcarbamoyl group, a substituted alkylcarbamoyl group, an arylcarbamoyl group, a substituted arylcarbamoyl group, a heterocyclylcarbamoyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, and carboxy, and

R^2 is a substituent selected from the group consisting of hydrogen, a branched or unbranched alkyl group, a substituted alkyl group, an alkyloxy group, an aryl group, a substituted aryl group, a heterocyclyl group, hydroxy, and

R^1 and R^2 together can represent a group of atoms completing a nucleus, and

each of R^3 and R^4 (same or different)

is a substituent selected from the group consisting of hydrogen, a halogen atom, a branched or unbranched alkyl group, a branched or unbranched alkyloxy group, an aralkyloxy group, an aryl group, an alkenyl group, an acylamido group, an alkylamino group, a hydroxy group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkyloxycarbonyloxy group, an aryloxycarbonyloxy group, an alkylthio group, an arylthio group, and a benzenesulphonyl group.

2. A photographic element according to claim 1, characterized in that said speed-increasing benzoxazine and benzothiazine derivatives are added in amounts ranging from 0.25 g to 8.0 g, per 1.5 mol of silver halide.

3. A photographic element according to claim 1 or 2, characterized in that said speed-increasing benzoxazine and benzothiazine derivatives have been dispersed with the aid of at least one known oil-former.

4. A photographic element according to any of claims 1 to 3, characterized in that said speed-increasing benzoxazine and benzothiazine derivatives are dispersed with the aid of di-n-butyl phthalate or tricresyl phosphate oil-former.

5. A photographic element according to claim 3 or 4, characterized in that said oil-former is used in an amount ranging from about 0.5 to about 2 parts by weight relative to the amount of the speed-increasing

benzoxazine and benzothiazine derivatives dispersed therewith.

6. A photographic element according to claim 5, characterized in that equal weights of said oil-former and said speed-increasing benzoxazine and benzothiazine derivatives are used.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 20 2261

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.5)
A	DE-A-3 529 934 (FUJI) * Page 16, compound 19 * ---	1-6	G 03 C 1/295 G 03 C 1/10
A	FR-A-2 013 284 (AGFA-GEVAERT) * Page 2, lines 26,33 * ---	1-6	
A	RESEARCH DISCLOSURE BULLETIN, PRODUCT LICENSING INDEX, no. 98, June 1972, pages 31,32, disclosure no. 9806, Havant, Hampshire, GB; "Photographic compositions and processes" * Whole document * -----	1-6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

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	20-06-1989	BUSCHA A.J.

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
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E : earlier patent document, but published on, or after the filing date
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