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SPECTRAL SENSITIZATION OF PHOTODEVELOPABLE SILVER HALIDE EMULSIONS

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U.S. Cl. 96—125 **10 Claims**

ABSTRACT OF THE DISCLOSURE

A photodevelopable direct-print radiation sensitive silver halide emulsion is described which comprises an iodine compound, a cadmium compound and an imidacarbocyanine spectrally sensitizing dye in which at least one of the benzorings carries one or more substituents characterized by a Hammet constant σ_p of at least 0.25, nitro being excluded. With these spectrally sensitized emulsions direct-print image records having a favourable image-discrimination and a low minimum density can be obtained.

The present invention relates to the spectral sensitization of photographic elements having a photodevelopable radiation-sensitive silver halide emulsion layer.

Photodevelopable silver halide elements possess desirable properties for high speed recording, such as high speed oscillographic recording, of events which occur in rapid sequence.

Photodevelopable silver halide materials for direct recording are radiation-sensitive materials in which a visible image can be obtained after an exposure to a high-intensity source of radiation has been initially utilized to form a latent image, by an additional exposure to a radiation of lower intensity such as diffuse daylight or artificial light. The secondary exposure, also called latensification, is an overall exposure including exposing the areas in which the initial latent image was formed as well as the surrounding background to an additional amount of radiation.

Photodevelopable silver halide emulsions can be orthochromatically and panchromatically sensitized for instance in view of their use with high pressure mercury vapour lamps and tungsten lamps. However, as compared with wet-development the spectrally sensitizing dyes used are generally not or incompletely bleached during photodevelopment so that the background areas of the image records are coloured and thus the minimum density is increased which results in less image discrimination

$$(D_{\text{max.}}-D_{\text{min.}}).$$

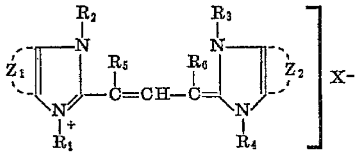
Moreover, the sensitizing effect of most of the common spectral sensitizing dyes, when used in photodevelopable silver halide emulsions, is reduced in that they are desorbed from the silver halide grains by the halogen acceptor used.

It has now been found that photodevelopable silver halide emulsions to which molecular iodine, a silver iodide sol and/or a compound which releases iodide ions in aqueous medium as well as a cadmium compound has been added, can be spectrally sensitized and yield direct-print image records having a favourable image-discrimination ($D_{\text{max.}}-D_{\text{min.}}$) and a low minimium density by using as spectral sensitizer an imidacarbocyanine dye in which at least one of the benzorings carries one or more substituents characterized by a Hammet constant σ_p of at least 0.25; the desensitizing nitro group being, however, excluded from said substituents.

To the photodevelopable silver halide emulsions according to the present invention molecular iodine, a silver iodide sol and/or a compound that releases iodide ions in aqueous medium such as inorganic and organic iodides, organic compounds with labile iodine atom and onium chloroiodates examples of which can be found among others in United Kingdom patent specification 1,160,956 are added. By the presence of these iodine compounds higher net densities and thus more contrasty images are obtained. The amount of iodine compound added to the emulsion may vary within wide limits. In general an amount from 0.01 g. to 20 g., preferably from 0.1 g. to 5 g. per mole of silver halide is applied.

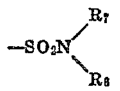
The spectrally sensitized photodevelopable silver halide emulsions of the invention also comprise a cadmium compound. These compounds are preferably inorganic water-soluble cadmium salts such as cadmium nitrate, cadmium iodide, cadmium chloride and especially cadmium bromide, but also include organo-cadmium compounds and cadmium complexes. The cadmium compounds suppress the sensitivity of the emulsion in the unexposed areas and thus reduce the background density on latensification. They are added to the emulsions after precipitation of the silver halide and prior to coating. They may be used in amounts varying between very wide limits usually from 1 to 20 g. and preferably from 5 to 15 g. of cadmium compound per mole of silver halide.

Particularly useful imidacrbocyanines for use according to the present invention are those corresponding to the formula:



wherein:

each of Z_1 and Z_2, the same or different, stands for the atoms necessary to complete a fused-on benzene nucleus or substituted benzene nucleus, at least one of Z_1 and Z_2 representing the atoms necessary to complete a fused-on benzene nucleus carrying one or more substituents characterized by a Hammet constant σ_p of at least 0.25, nitro being excluded, for example a cyano group, an alkoxy carbonyl group such as ethoxycarbonyl, a fluorosulphonyl group, an alkylsulphonyl such as methylsulphonyl or a substituted alkylsulphonyl group such as alkylsulphonyl wherein the alkyl group is substituted by one or more fluorine and/or chlorine atoms, an alkylsulphinyl group or substituted alkylsulphinyl group such as alkylsulphinyl wherein the alkyl group is substituted by one or more fluorine and/or chlorine atoms, a trifluoromethyl group, a trifluoromethoxy group, a trifluoromethylthio group, a difluoromethylthio group, and preferably a fluorsulphonyl group or sulphamoyl group of the formula



$$-SO_2N\begin{matrix} R_7 \\ R_8 \end{matrix}$$

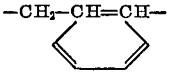
wherein each of R_7 and R_8, the same or different, stands for hydrogen or a saturated or unsaturated aliphatic group including a substituted aliphatic group such as alkyl, preferably C_1–C_5 alkyl, cycloalkyl, e.g. cyclohexyl or allyl, or R_7 together with R_8 represent the atoms necessary to close a heterocyclic ring such as pyrrolidine, piperidine, piperazine, morpholine, etc.

each of R_1, R_2, R_3 and R_4, the same or different, stands for a substituent of the type contained in cyanine dyes on the cyanine nitrogen atom, for example an aliphatic group including a saturated aliphatic group, an unsaturated aliphatic group and a cycloaliphatic group such as alkyl, aralkyl, allyl and cycloalkyl or an aromatic group, which groups may carry substituents; more particularly an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl or isobutyl, a substituted alkyl group such as β-hydroxyethyl, β-acetoxyethyl, carboxymethyl, carboxyethyl, sulphoethyl, sulphopropyl, sulphobutyl, sulphatopropyl, sulphatobutyl, phosphonoethyl, phosphonopropyl phosphonobutyl, the group

$$—A—CO—O—B—SO_2—OH$$

wherein A and B have the same significance as set forth in United Kingdom patent specification 886,271 such as sulphocarbomethoxymethyl, ω - sulphocarbopropoxymethyl, ω-sulphocarbobutoxymethyl, and p-(ω-sulphocarbobutoxy)-benzyl, the group —A—W—NH—V—B as described in United Kingdom patent specification 904,332 wherein each of W and V represents carbonyl, sulphonyl or a single bond, at least one of W and V being sulphonyl, A represents an alkylene group e.g. a C_1–C_4 alkylene group and B represents hydrogen, alkyl, substituted alkyl, amino, substituted amino e.g. acylamino, diethylamino with the proviso however that B does not represent hydrogen when V stands for carbonyl or sulphonyl, the group AWNHVB being exemplified by N-methylsulphonyl)-carbamylmethyl, γ-(acetylsulphamyl)-propyl, and δ-(acetylsulphamyl)-butyl, an aralkyl group such as a benzyl, a substituted aralkyl group such as carboxybenzyl and sulphobenzyl, a cycloalkyl group such as cyclohexyl, an allyl group, an aryl group such as phenyl, and a substituted aryl group such as carboxyphenyl,

each of R_5 and R_6 stands for hydrogen or R_5 together with R_2 and/or R_6 together with R_3 represent the atoms of the type described in French patent specification 1,337,260 necessary to form a fused-on ring such as $—CH_2—CH_2—$, $—(CH_2)_3—$,

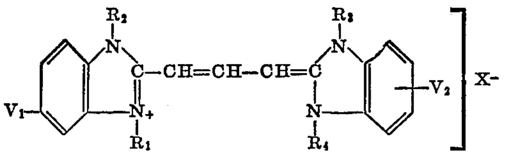


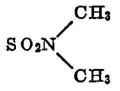
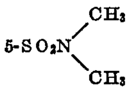
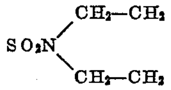
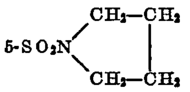
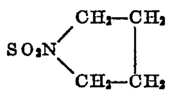
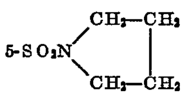
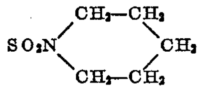
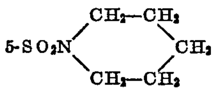
and $—O—CH_2—CH_2—$, and

X^- stands for an anion of the type contained in cyanine dye salts such as halide, perchlorate, methyl sulphate, benzene sulphonate, p-toluene sulphonate, etc. but does not exist when one of R_1–R_4 itself contains an anionic group in which case the dye is a betaine dye salt.

Representative examples of imidacarbocyanines suitable for use in accordance with the present invention are listed in the following table.

TABLE



Dye	V_1	R_1	R_2	V_2	R_3	R_4	X
1	SO_2CH_3	C_2H_5	C_2H_5	$5\text{-}SO_2CH_3$	C_2H_5	C_2H_5	I
2	SO_2CHF_2	C_2H_5	C_2H_5	$5\text{-}SO_2CHF_2$	C_2H_5	C_2H_5	I
3	SO_2CF_3	C_2H_5	C_2H_5	$5\text{-}SO_2CF_3$	C_2H_5	C_2H_5	I
4	SO_2CF_3	C_2H_5	$(CH_2)_4—SO_2—N.COCH_3$	$5\text{-}SO_2CF_3$	C_2H_5	$(CH_2)_4SO_2NHCOCH_3$	
5	SO_2CF_2CHFCl	C_2H_5	C_2H_5	$5\text{-}SO_2CF_2CHFCl$	C_2H_5	C_2H_5	I
6	SO_2F	C_2H_5	C_2H_5	$5\text{-}SO_2F$	C_2H_5	C_2H_5	I
7	$SO_2NHC_2H_5$	C_2H_5	C_2H_5	$5\text{-}SO_2NHC_2H_5$			
8	 $SO_2N(CH_3)_2$	CH_3	CH_3	 $5\text{-}SO_2N(CH_3)_2$	CH_3	CH_3	I
9	 $SO_2N(CH_2—CH_3)_2$	CH_3	C_2H_5	5, 6-diCl	C_2H_5	C_2H_5	I
10	Same as above	C_2H_5	C_2H_5		C_2H_5	C_2H_5	I
11	$—COOC_2H_5$	C_2H_5	C_2H_5	$5\text{-}COOC_2H_5$	C_2H_5	C_2H_5	I
12	$—COCH_3$	C_2H_5	C_2H_5	$5\text{-}COCH_3$	C_2H_5	C_2H_5	I
13	CN	C_2H_5	C_2H_5	5-CN	C_2H_5	C_2H_5	I
14	CN	C_2H_5	$(CH_2)_2OCOCH_3$	5-CN	C_2H_5	$(CH_2)_2OCOCH_3$	Br
15	CN	C_2H_5	$(CH_2)_4SO_2NHCOCH_3$	5-CN	C_2H_5	C_2H_5	Br
16	SO_2CH_2Cl	CH_3	C_2H_5	$5\text{-}SO_2CH_2Cl$	CH_3	C_2H_5	I
17		CH_3	C_2H_5		CH_3	$(CH_2)_3SO_3^-$	
18	Same as above	CH_3	$(CH_2)_3SO_3^-$	Same as above	CH_3	$(CH_2)_3SO_3^-$	
19		CH_3	CH_3		CH_3	CH_3	I
20	Same as above	CH_3	$(CH_2)_3SO_3^-$	Same as above	CH_3	C_2H_5	
21	SO_2CH_2Cl	C_2H_5	C_2H_5	$5\text{-}SO_2CH_2Cl$	C_2H_5	C_2H_5	I
22	CF_3	C_2H_5	C_2H_5	C_2H_5	C_2H_5	C_2H_5	I
23	$SOCF_3$	C_2H_5	C_2H_5	$SOCF_3$	C_2H_5	C_2H_5	I

The methine dye salts for spectrally sensitizing photodevelopable silver halide emulsions in accordance with the present invention may be used in amounts varying between very wide limits. Generally they are used in amounts comprised between 1 mg. and 1000 mg. preferably between 50 mg. and 500 mg. per mole of silver halide.

The methods of incorporating the dyes in the emusion are simple and well known to those skilled in the art of emulsion making. They are generally added to the emulsion in the form of a solution in a suitable solvent e.g. an alcohol such as methanol or a mixture of alcohol and water. The solvent must of course be compatible with the emulsion and substantially free from any deleterious effect on the photodevelopable material.

The sensitizing dyes of use according to the present invention can be incorporated in the emulsion at any stage of emulsion preparation and should be uniformly distributed throughout the emulsion. They are preferably incorporated just before coating of the emulsion on a support.

The silver halides used in the preparation of the photodevelopable radiation-sensitive silver halide emulsions of the present invention, include silver bromide, silver bromoiodide, silver chlorobromide and silver chlorobromoiodide emulsions. Silver chlorobromide and silver bromide emulsions which may comprise minor amounts of silver iodide, preferably not more than 5 mole percent relative to the total amount of silver halide, are favoured.

The photodevelopable radiation-sensitive emulsions form latent images predominantly inside the silver halide grains. A silver halide emulsion that mainly or entirely forms an internal latent image and only to a little extent an external latent image is an emulsion in which only a few or no exposed grains at all are developable into silver by a developing solution that cannot act as a developer for a latent image inside the grains i.e. a so-called "surface" developer, such as:

	G.
p-Hydroxyphenyl glycine	10
Sodium carbonate (cryst.)	100
Water to 1000 ccs.	

and wherein the exposed grains are well developable to silver by a developing solution that acts as a developer for latent image inside the grains i.e. a so-called "internal" developer such as the following solution:

	G.
Hydroquinone	15
Monomethyl-p-aminophenol sulphate	1.5
Sodium sulphite (anhydrous)	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulphate (cryst.)	20
Water to 1000 ccs.	

By a silver halide emulsion that mainly forms internal latent image and little external latent image there is more particularly meant a silver halide emulsion, a test layer of which upon exposure to a light intensity scale for a fixed time between $1/100$ and 1 sec. and development for 3 min. at 20° C. in the above "internal" developer, exhibits a maximum density at least 5 times the maximum density obtained when an identical test layer of the said silver halide emulsion is equally exposed and then developed for 4 min. at 20° C. in the above "surface" developer.

Silver halide emulsions that meet the above requirement are generally not or only slightly chemically ripened silver halide emulsions, since the extent of the surface latent image-forming capability increases with the degree of chemical ripening. After precipitation of the silver halide grains the emulsion may or may not be, but preferably is washed.

The emulsions may be prepared according to all known and conventional techniques of emulsion preparation. A method according to which emulsions are prepared and which has proven to be particularly suitable for the purpose of the invention is the so-called conversion method according to which an emulsion of a silver salt that has a higher degree of water solubility than silver bromide is converted into a silver chlorobromide or silver bromide emulsion that occasionally contains small amounts of silver iodide. This conversion is carried out preferably very slowly for instance by several consecutive steps.

Gelatin is preferably used as the hydrophilic colloid binder but other colloidal materials such as colloidal albumin, cellulose derivatives and synthetic resins e.g. polyvinyl compounds or mixtures thereof with gelatin can also be used.

The light-sensitive silver halide emulsion may contain all kinds of ingredients which are generally known in the art of photodevelopable emulsion preparation. The emulsion may contain in addition to the specific ingredients as set forth above hardening agents e.g. formaldehyde, coating aids e.g. saponine, plasticizers e.g. glycerol, development accelerators, compounds that render the material resistant to wrinkling and less brittle, compounds that stabilize the photodeveloped image e.g. thiocyanate such as potassium thiocyanate, etc.

It is common practice in the preparation of photodevelopable silver halide emulsions to utilise halogen acceptors. A wide variety of compounds has been proposed for use as halogen acceptors such as N-containing halogen acceptors of the thiourea type, of the hydrazine type, thiouracil, urazole and thiourazole halogen acceptors, mercapto-triazoles, mercapto-imidazoles, imidazolidinethiones, mercaptotriazines, hydrazothiocarbonamide, thiosemicarbazide; further aromatic mercaptans such as thiosalicylic acid, phenylenediamines, aminophenols, hydroquinones, 3-pyrazolidones, nitriles, phenols, and the like hologen acceptors well known to those skilled in the art including stannous salts such as stannous chloride. For a detailed survey of halogen acceptors suitable for use in photodevelopable radiation-sensitive silver halide emulsions, which can be spectrally sensitized according to the present invention, there can be referred to U.S. patent specification 3,287,137. The use of halogen acceptors, however, is not necessary to the present invention. Indeed, even in the absence of halogen-acceptors the emulsions spectrally sensitized in accordance with the present invention yield images with favourable image-discrimination.

The photodevelopable radiation-sensitive silver halide elements according to the invention may comprise any of the wide variety of supports in accordance with usual practice.

Examples of suitable supports are paper, polyethylene-coated paper, polypropylyene-coated paper, cellulose acetate film, polyvinyl acetal film, polyestyrene film, polyethylene terephthalate film, films of other resinous materials, glass and metal supports.

In the preparation of photodeveloped images by means of the spectrally sensitized photodevelopable material according to the present invention the radiation-sensitive silver halide element is first image-wise exposed to radiation in the spectrum range in which the silver halide is sensitive to such an extent that a latent image is formed in the silver halide material but taking care that the silver halide is not caused to print-out. Broadly speaking, such an exposure can be effected with high as well as with low intensity radiation. However, the image-wise exposure mostly occurs with high-intensity actinic radiation, e.g. from Xenon tubes, U.V.-lamps or high pressure mercury vapour lamps. The image-wise exposure may occur by means of light-spots or spots of another actinic radiation (trace beam; oscilloscope traces). The high-intensity radiation source used for the initial exposure may be an actinic light or other electromagnetic radiation of either visible or invisible wavelength, X-rays, gamma rays or an electron beam.

The sharpness of the recorded trace or image may be further increased by a short preliminary and overall exposure of the photodevelopable radiation-sensitive material according to the invention to ordinary light, e.g. daylight, prior to exposing the material image-wise to the high-intensity radiation. Indeed, by this short prelimary exposure the gradation in the toe of the characteristic curve and the contrast or net density of the recorded trace of image are increased.

It may be advantageous in the formation of the photodeveloped images, to supply heat to the latent-image containing layer before and/or during photodevelopment so that the recorded images become more rapidly visible. This can be done for instance by contacting the material with a hot plate, say at a temperature comprised between 80 and 200° C. in the photodevelopment step. A probable explanation of the favourable effect of supplying heat before and/or during photodevelopment has been given by Jacobs, Phot. Sci. and Eng., vol. 5, No. 1, 1961. It would appear that by this heat treatment the propensity of the non-image or background areas to print-out i.e. to increase in density upon exposure to radiation is greatly reduced so that the intensity of the secondary exposure can be increased, without producing fog.

Some oscillographs operate according to this principle: after the latent-image exposure the material is passed over a heated plate while being overall exposed so that a visible image is produced almost immediately. By applying heat in this way when high writing speeds and thus high paper transport speeds are used it is not necessary to expose considerable lengths of material to ambient light at the same time, which would lead to a handling problem.

If desired the material may be chemically developed and fixed during or after the photodevelopment by means of the common developing and fixing solutions. A mere fixation of the photodeveloped element without a preliminary chemical development sufficies if a non-acidic fixer is used. The image-wise exposed photographic element according to the present invention may, of course, also be developed and then fixed without a photodevelopment being carried out.

The following examples ilustrate the present invention.

EXAMPLE 1

A light-sensitive photographic silver bromide emulsion of the light-developable type, i.e. that mainly forms an internal latent image and only to a little extent an external latent image was prepared by conversion of a silver chloride emulsion into a silver bromide emulsion. Said silver bromide emulsion was prepared so that an amount of silver bromide equivalent to 130 g. of silver nitrate was present per kg. of emulsion.

The usual emulsion ingredients and coating aids were incorporated into the emulsion and in addition thereto 8 g. of cadmium bromide was added per kg. for reducing the background density.

The emulsion obtained was divided into three aliquot portions. To two of these portions the additives listed in the table below were added.

The three emulsion samples were coated on conventional photographic paper supports such that an amount of silver halide equivalent to 4 g. of silver nitrate was present per sq. m. of light-sensitive material.

The three light-sensitive materials obtained were subjected to the following identical successive treatments.

(1) They were exposed in a flash-sensitometer "Mark VI" of Edgerton, Germeshausen and Grier for 10^{-4} sec. through a step-wedge with a constant of 0.30.

(2) The exposed materials were photo-developed for 15 min. by exposure to ordinary office fluorescent lights with a total light intensity of 240 lux whereupon the

density of the image-areas ($D_{max.}$) and non-image areas ($D_{min.}$) were measured in a MacBeth reflection densitometer.

The values obtained for the maximum and minimum densities as well as the image discrimination

$$(D_{max.})-D_{min.}=\Delta D)$$

are listed in the table below. The number of the steps of the wedge that were recorded is also listed in the table hereinafter. This number is a measure of the sensitivity of the three emulsion samples.

TABLE

Additives per kg. emulsion	$D_{max.}$	$D_{min.}$	ΔD	Number of steps
	0.09	0.09		
100 mg. of dye 3	0.23	0.13	0.10	4
100 mg. of dye 3+10 ml. of 5% by weight aqueous potassium iodide	0.55	0.19	0.36	6.5

The above results show that by the combined use of cadmium bromide, spectrally sensitizing dye 3 and potassium iodide a favourable image discrimination is obtained even in the absence of a halogen acceptor.

EXAMPLE 2

To an emulsion as described in Example 1 the usual emulsion ingredients and coating aids were added and in addition thereto per kg.:8 g. of cadmium bromide for reducing the background density and 10 ml. of a 5% by weight aqueous solution of potassium iodide; no halogen acceptor was added to the emulsion.

The emulsion was divided into several aliquot portions. To these portions were added the spectrally sensitizing dyes listed in the table below in an amount of 100 mg. per kg. emulsion.

As in Example 1, the emulsions were coated on a paper support whereupon the materials formed were exposed and photodeveloped in the same way as in Example 1. The results obtained after photodevelopment for 15 min. are listed in the table below.

TABLE

Dye	$D_{max.}$	$D_{min.}$	ΔD	Number of steps
1	0.55	0.19	0.36	6
2	0.55	0.22	0.33	6
3	0.57	0.21	0.36	6.5
4	0.47	0.17	0.30	4
5	0.59	0.20	0.39	6.5
6	0.63	0.23	0.40	6
7	0.57	0.19	0.38	6.5
8	0.53	0.18	0.35	6
9	0.55	0.19	0.36	5.5
10	0.51	0.18	0.33	5.5
11	0.55	0.19	0.36	6
12	0.55	0.21	0.34	5.5
13	0.53	0.19	0.34	6
14	0.49	0.17	0.32	5
15	0.51	0.17	0.34	5
16	0.57	0.19	0.38	6
17	0.53	0.19	0.34	5
18	0.50	0.17	0.33	5.5
19	0.54	0.18	0.36	6.5
20	0.55	0.19	0.36	5.5

EXAMPLE 3

An emulsion as described in Example 2, to which cadmium bromide and potassium iodide was added, was divided into three aliquot portions A, B, and C. To these emulsion portions were added per kg. 100 mg. of the spectrally sensitizing dye 3. In addition thereto 125 mg. of 6,6-dimethyl-3-thio-1,6-dihydro - as - triazine-3,5(2H, 4H)dione were added per kg. to emulsion portions B and C as halogen acceptor and to emulsion portion C 4 g. of potassium thiocyanate were added per kg. for stabilizing the photodeveloped image.

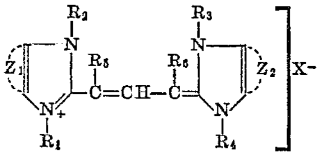
As in Example 1, the emulsion portions were coated on a paper support whereupon the materials formed were exposed and photodeveloped in the same way as in Example 1. The results obtained after photodevelopment for 15 min., 2 days, and 8 days respectively are listed in the table below.

Emulsion	$D_{max.}$				$D_{min.}$				ΔD				Number of steps			
	15 min.	2 d.	4 d.	8 d.	15 min.	2 d.	4 d.	8 d.	15 min.	2 d.	4 d.	8 d.	15 min.	2 d.	4 d.	8d
A	0.61	0.39	0.34	0.31	0.23	0.19	0.19	0.19	0.38	0.20	0.15	0.12	6.5	5	4.5	3.5
B	0.67	0.43	0.38	0.33	0.25	0.20	0.18	0.19	0.42	0.23	0.20	0.14	6.5	5.5	5	4.5
C	0.68	0.56	0.51	0.50	0.25	0.30	0.27	0.28	0.43	0.26	0.24	0.21	6	6	5.5	5.5

The above results show that even in the absence of a halogen acceptor (emulsion A) a favourable image-discrimination is obtained and that slightly improved results are obtained in the presence of a halogen acceptor (emulsion B). By the presence of the potassium thiocyanate (emulsion C) the photodeveloped image shows a markedly improved stability.

We claim:

1. A photodevelopable direct-print radiation-sensitive silver halide emulsion to which an iodine compound selected from the group consisting of molecular iodine, a silver iodide sol and a compound which releases iodide ions in aqueous medium as well as a cadmium compound have been added wherein said emulsion is spectrally sensitized by the addition of a dye corresponding to the formula:



wherein:

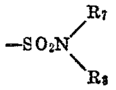
each of Z_1 and Z_2, the same or different, stands for the atoms necessary to complete a fused-on benzene nucleus at least one of Z_1 and Z_2 representing the atoms necessary to complete a fused-on benzene nucleus carrying one or more substituents characterized by a Hammet constant σ_p of at least 0.25 and selected from the group consisting of cyano, an alkoxycarbonyl group, fluorosulphonyl, an alkylsulphonyl group, an alkylsulphinyl group, trifluoromethyl, trifluoromethoxy, trifluoromethylthio, difluoromethylthio, and a sulphamoyl group,

each of R_1, R_2, R_3 and R_4, the same or different, stands for an aliphatic group or an aromatic group,

each of R_5 and R_6 stands for hydrogen or R_5 together with R_2 and/or R_6 together with R_3 represent the atoms necessary to complete a fused-on ring, and

X^- stands for an anion but does not exist when R_1, R_2, R_3 or R_4 comprises an anionic group.

2. A photodevelopable emulsion according to claim **1**, wherein at least one of Z_1 and Z_2 represents the atoms necessary to complete a fused-on benzene nucleus carrying a fluorosulphonyl group or a sulphamoyl group of the formula



$$-SO_2N\begin{matrix} R_7 \\ R_8 \end{matrix}$$

wherein each of R_7 and R_8, the same or different, stands for hydrogen or a saturated or unsaturated aliphatic group or R_7 together with R_8 represent the atoms necessary to complete a heterocycle.

3. A photodevelopable emulsion according to claim **1**, wherein the said iodine compound is potassium iodide.

4. A photodevelopable emulsion according to claim **1**, wherein the said cadmium compound is cadmium bromide.

5. A photodevelopable emulsion according to claim **1**, wherein the said emulsion also comprises potassium thiocyanate.

6. A photodevelopable emulsion according to claim **1**, wherein the same emulsion forms latent images predominantly inside the silver halide grains.

7. A photodevelopable emulsion according to claim **6**, wherein the silver halide is silver bromide.

8. A photodevelopable emulsion according to claim **1**, wherein the emulsion also comprises a halogen acceptor.

9. A photodevelopable emulsion according to claim **1**, wherein the said dye is used in an amount comprised between 1 mg. and 1000 mg. per mole of silver halide.

10. A photodevelopable emulsion according to claim **1** wherein each of R_1, R_2, R_3 and R_4 are lower alkyl and R_5 and R_6 are hydrogen.

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