United States Patent [19]

Ikenoue et al.

[11] **3,909,271**

[45] **Sept. 30, 1975**

[54] HEAT DEVELOPABLE PHOTOGRAPHIC MATERIAL CONTAINING SENSITIZERS

[75] Inventors: **Shinpei Ikenoue; Takao Masuda,** both of Saitama, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.,** Minami-ashigara, Japan

[22] Filed: **Jan. 31, 1974**

[21] Appl. No.: **438,320**

[30] **Foreign Application Priority Data**

Jan. 31, 1973 Japan 48-12587

[52] **U.S. Cl.** .... **96/95;** 96/109; 96/61 R; 96/114.1; 96/114.6

[51] **Int. Cl.^{2}** **G03C 1/06**

[58] **Field of Search** .... 96/67, 114.1, 114.6, 107, 96/109, 61 R; 117/36.7, 36.8

[56] **References Cited**

UNITED STATES PATENTS

3,071,464	1/1963	Chalkley	96/107
3,449,122	6/1969	Kretchman et al.	96/109
3,457,075	7/1969	Morgan et al.	96/114.1
3,594,171	7/1971	Kimura et al.	96/109
3,645,739	2/1972	Ohkubo et al.	96/114.1
3,770,448	11/1973	Poot et al.	96/114.1
3,799,779	3/1974	Burleigh	96/114.1

Primary Examiner—Norman G. Torchin
Assistant Examiner—Judson R. Hightower
Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57] ABSTRACT

A sensitized heat developable photographic material having at least one photosensitive layer on a support, said layer containing the following components:

a. an organic silver salt,

b. a catalytic amount of a photosensitive silver halide or a compound which reacts with the organic silver salt (a) to produce a photosensitive silver halide,

c. a reducing agent,

d. a binder, and

e. at least one sensitizer as hereinafter described.

The compounds (e) are sensitizers providing particularly excellent sensitizing effects.

15 Claims, No Drawings

HEAT DEVELOPABLE PHOTOGRAPHIC MATERIAL CONTAINING SENSITIZERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to heat developable photographic materials, and, in particular, to those having at least one photosensitive layer of especially high sensitivity.

2. Description of the Prior Art

A photographic process using silver halides is the process which has heretofore been most widely practiced due to the excellent photographic properties thereof, such as high sensitivity and good gradation, over all other processes such as an electrophotographic process or a diazo-photographic process. However, silver halide photographic materials used in the process are developed with a developer after image-wise exposure, and then they are subjected to several after-treatments such as stopping, fixation, washing with water or stabilization so that the developed images do not discolor or deteriorate under normal illumination or so that the non-developed part (hereunder referred to as "background") is not blackened. Accordingly, these treatments require superfluous time and labor, and in addition, danger to the human body on exposure to the chemicals used in these treatments and troublesome problems that the interior of processing areas and the hands and clothes of operators become stained occur. Therefore, in the photographic process using silver halides, it is extremely desired to improve the treatment thereof so that the treatment can be carried out in a dry state without solution treatment and that the treated image can be kept stable. For this, various efforts have heretofore been made.

A first method is the so-called one-bath development and fixation method as described in, for example, U.S. Pat. No. 2,875,048, British Pat. No. 954,453 and German Pat. No. 1,163,142, where the two operations of development and fixation in the conventional silver halide photographic process are carried out in one bath. A second method is to try to change the wet-type treatment which has been used in the up-to-date silver halide photographic process, to a dry-type treatment, for example, as described in German Pat. No. 1,174,159, British Pat. Nos. 943,476 and 951,644, etc. A third method is to try to use, as photosensitive elements, a combination of a main component of a long chain aliphatic carboxylic acid silver salt, such as silver behenate, or another silver salt such as silver saccharin or silver benzotriazole, and a catalytic amount of a silver halide, for example, as described in Japanese Patent Publication No. 22185/70, U.S. Pat. Nos. 3,152,904, 3,457.075, and 3,635,719, British Pat. No. 1,205,500, etc.

This invention belongs to the third method of the above described methods.

Unfortunately sufficient photosensitivity has not as yet been attained in conventional heat developable photographic materials, for example, those comprising compositions of a fatty acid silver salt, a reducing agent and a catalytic amount of silver halide.

Regarding the conventional techniques for sensitization of conventional heat developable photographic materials, Japanese Patent Publication No. 4924/68 described above, which belongs to this third method, discloses that known merocyanine dyes are effective as a so-called optical sensitizer to silver halide emulsions. In addition, Japanese Patent Publication No. 4921/68 discloses that Eosine, Erythrocin and uranine are effective thereto. However, every optical sensitizer which is effective for silver halide emulsions, is, in general, not always effective for every heat developable photographic material, and it is difficult to predict what kind of sensitizer of what structure is effective for heat developable photographic materials. Furthermore, the sensitizing effect of the above described known sensitizers, the merocyanine dye, is not very good, and in addition, Eosine, Erythrocin and uranine and defective in that, although they have a sensitizing effect, images of low Dmax and severe fog are produced therewith.

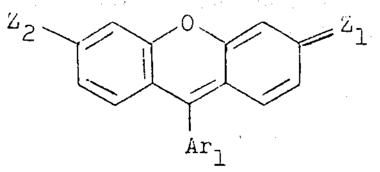
SUMMARY OF THE INVENTION

The present inventors have found after various studies on sensitizers that the compounds of formulae (I) through (IV) as described below have especially excellent sensitizing effect to heat developable photographic materials of this invention, and further they produce images of high Dmax and less fog.

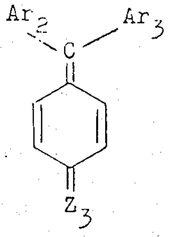
Therefore, an object of this invention is to provide heat developable photographic materials having at least one sensitized photosensitive layer.

More precisely, the present invention provides a sensitized heat developable photographic material having at least one photosensitive layer on a support, this layer containing the following components:

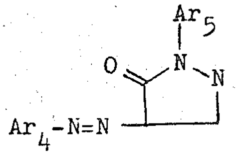
a. an organic silver salt,
b. a catalytic amount of a photosensitive silver halide or a compound which reacts with the organic silver salt (a) to produce a photosensitive silver halide.
c. a reducing agent,
d. a binder, and
e. at least one compound of the following formulae:



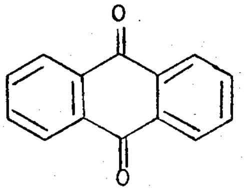
(I)



(II)

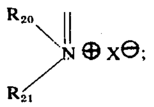


(III)

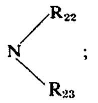


(IV)

wherein Z_1 and Z_3 each represents =O or



Z_2 represents —OM or



Ar_1, Ar_2, Ar_3, Ar_4 and Ar_5 each represents an unsubstituted or substituted aryl group;

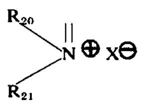
$X^{\ominus}$ represents an anion;

R_{20}, R_{21}, R_{22} and R_{23} each represents an unsubstituted or substituted alkyl or aryl group; and with the proviso that when Z_1 is =O, Z_2 is —OM, and Ar_1 does not contain a halogen substituent, and the nuclei in the formula (I) contain two halogen substituents;

Ar_1 contains at least one substituent of SO_3M and COOM; at least one of Ar_2 and Ar_3, and at least one of Ar_4 and Ar_5 each contains at least one substituent of SO_3M and COOM;

the formula (IV) contains at least one substituent of SO_3M and COOM in the nuclei or in the substituent(s) on the nuclei;

M represents a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, or an NH_4 group and each nucleus of the formulae (I) through (IV) can further contain additional substituent(s) other than the above defined substituents and the radical

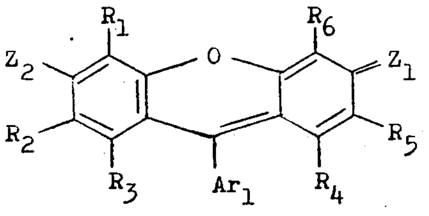


can be in the form of an inner salt.

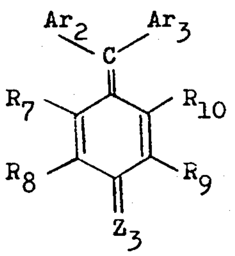
DETAILED DESCRIPTION OF THE INVENTION

Examples of aryl groups represented by Ar_1 through Ar_5 of the above described general formulae are unsubstituted or substituted phenyl groups and unsubstituted or substituted α- and β-naphthyl groups. Preferred substituents are alkyl groups (e.g., methyl, ethyl, isopropyl, butyl, etc. groups), halogen atoms (e.g., Cl, Br, I atoms), hydroxy groups, SO_3M groups, COOM groups, aryl groups (e.g., phenyl, tolyl, etc., groups), nitro groups, amino groups, acyl groups (e.g., acetyl, propionyl, etc., groups), alkoxy groups (e.g., ethoxy, methoxy, etc. groups), etc., with M having the same meaning as defined above. Examples of alkali metals represented by the above M are Li, Na, K, Rb, etc., and examples of alkaline earth metals are Ca, Mg, Ba, etc. An anion represented by $X^{\ominus}$ is, for example, a halogen ion, a sulfate ion, a nitrate ion, etc.

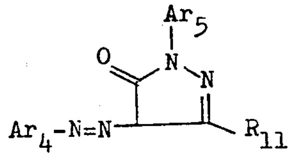
Preferred compounds of the above described formulae (I) through (IV) are those of the following formulae (I)′ through (IV)′.



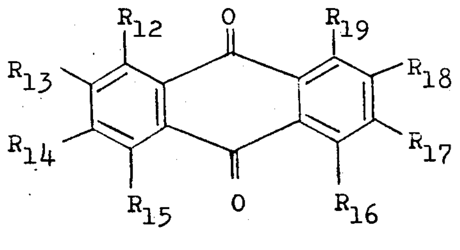
(I')



(II')



(III')



(IV')

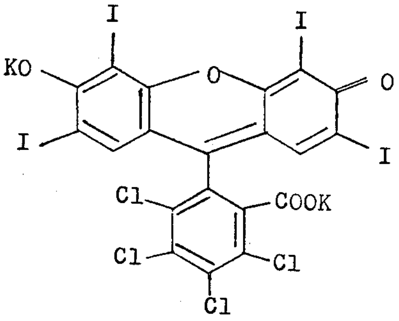
In the above formulae, R_1 through R_9, R_{13}, R_{14}, R_{17} and R_{18} each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, an aryl group, a halogen atom, a nitro group, a hydroxyl group, an SO_3M group, a COOM group, an alkoxy group, an acyl group and an amino group; and when Z_1 is =O, Z_2 is —OM and Ar_1 does not contain a halogen substituent, but two of these R_1 through R_6 substituent are halogen atoms; R_{11} represents a hydrogen atom, an alkyl group or a COOM group; R_{12}, R_{15}, R_{16} and R_{19} each represents a member selected from the group consisting of a hydrogen atom, an amino group, an alkylamino group, an arylamino group, an alkyl group, a halogen atom, a hydroxyl group, an SO_3M group and a

COOM group, and at least one of these R_{12} through R_{19} is a group having a SO_3M group and/or a COOM group, with M having the same meaning as defined above.

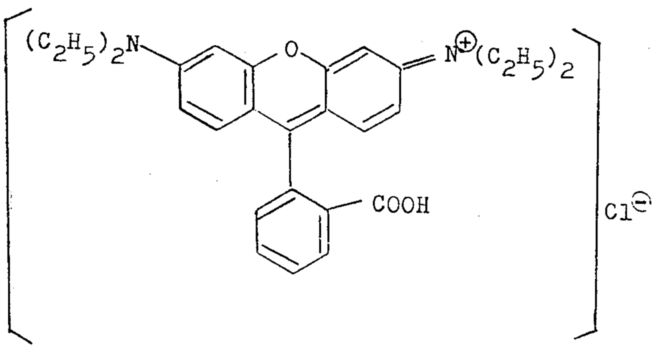
The alkyl group, alkoxy group, acyl group and alkylamino group represented by the above described symbols Ar_1 through Ar_5 and R_1 through R_{19} have in general 1 to 8, preferably 1 to 4, carbon atoms. Examples of substituents of the above described aryl groups and the groups R_1 through R_{19} are a methyl group, an ethyl group, an isopropyl group, a t-butyl group, an ethoxy group, an acetyl group, a dimethylamino group, etc. Alkyl groups represented by R_{20} through R_{23} have in general 1 to 8, preferably 1 to 4, carbon atoms, and examples thereof are a methyl group, an ethyl group, an isopropyl group, a butyl group, etc. Suitable substituents of the alkyl group, are, for example, a phenyl group or a sodium sulfophenyl group. Suitable substituents of the aryl groups represented by R_{20} through R_{23} are, for example, a phenyl group, a sodium sulfophenyl group, and a tolyl group.

Representative compounds suitable for the present invention are described below.

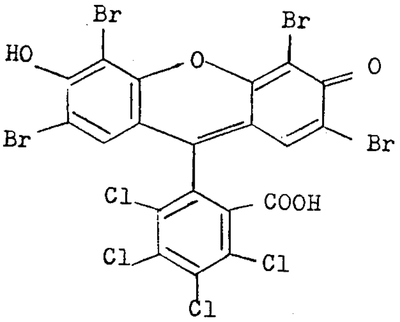
(1)



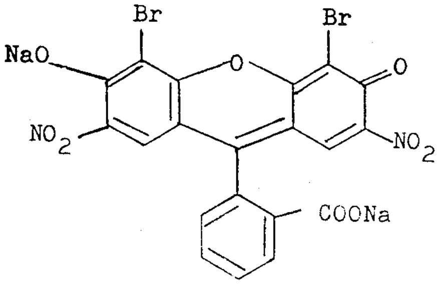
(2)



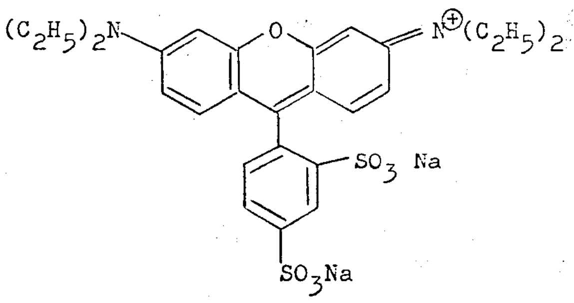
(3)



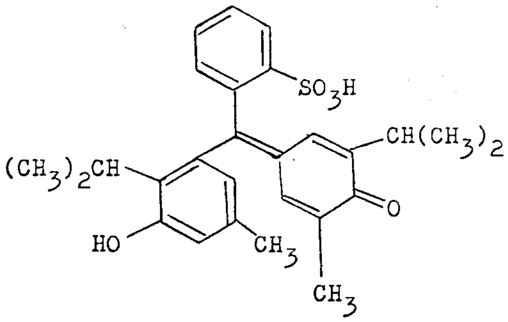
(4)



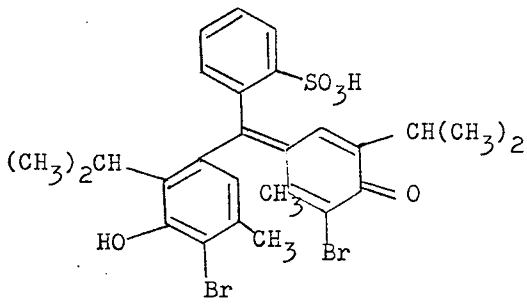
(5)


(C2H5)2N
O
N⊕(C2H5)2
SO3 Na
SO3Na

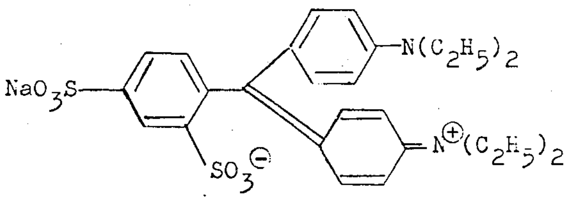
(6)


SO3H
CH(CH3)2
(CH3)2CH
O
HO
CH3
CH3

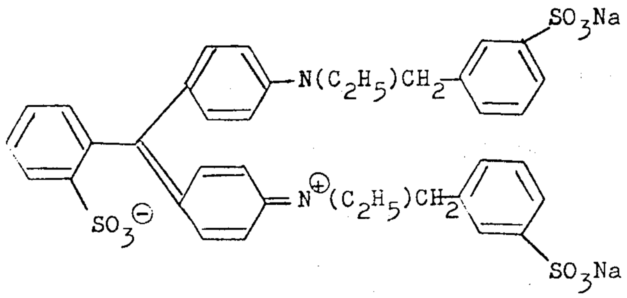
(7)


SO3H
CH(CH3)2
(CH3)2CH
CH3
O
HO
CH3
Br
Br

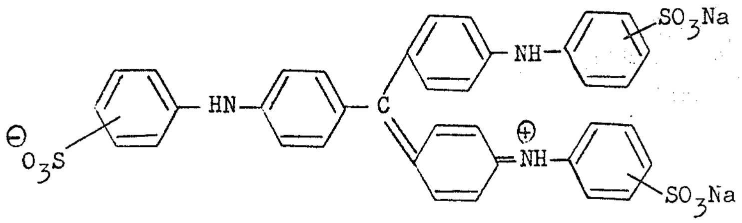
(8)


N(C2H5)2
NaO3S
N⊕(C2H5)2
SO3⊖

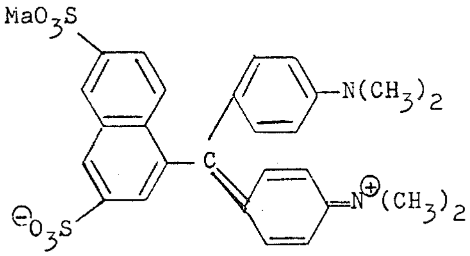
(9)


SO3Na
N(C2H5)CH2
N⊕(C2H5)CH2
SO3⊖
SO3Na

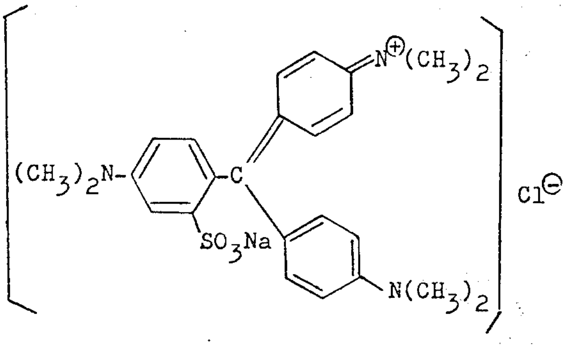
(10)



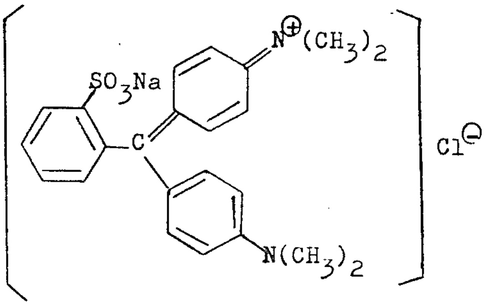
(11)



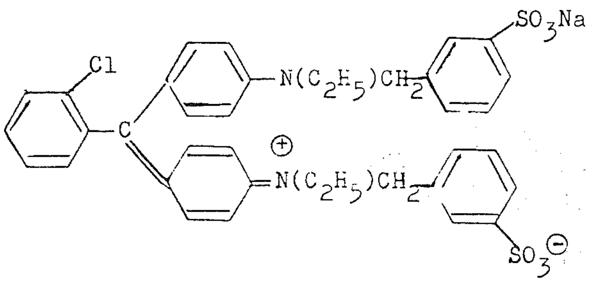
(12)



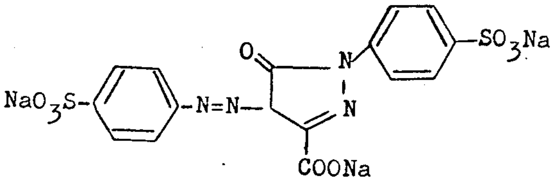
(13)



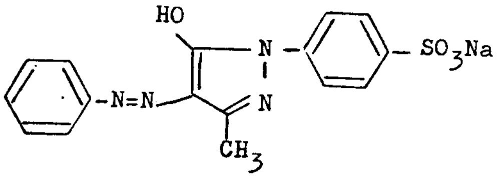
(14)



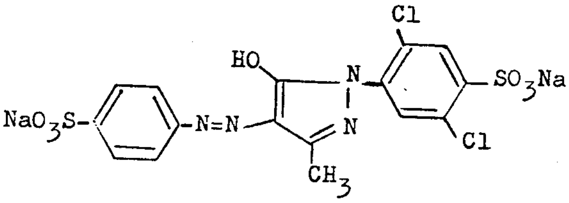
(15)



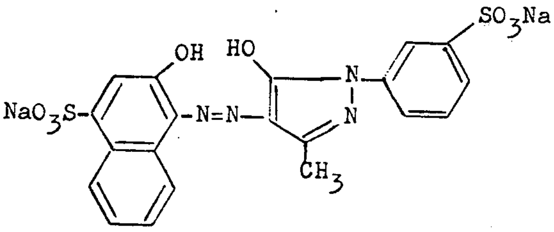
(16)



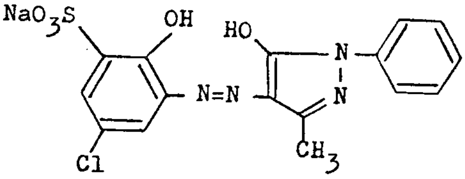
(17)



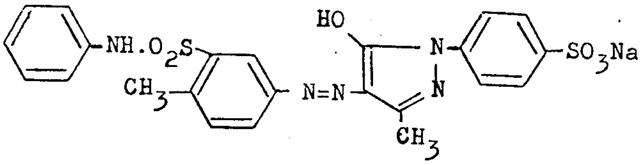
(18)



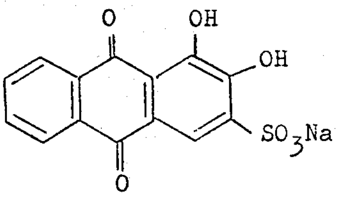
(19)



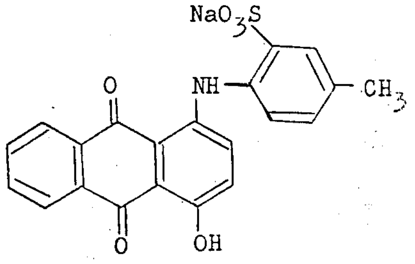
(20)



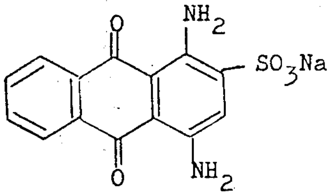
(21)



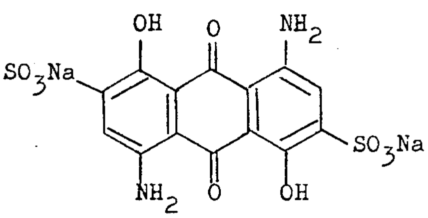
(22)



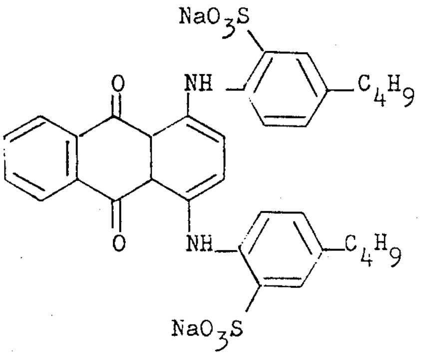
(23)



(24)



(25)



The amount of the component (e), which is a compound effective as a sensitizer of the present invention, which is added is suitably about 10^{-6} to 10^{-2} mole per 1 mole of organic silver salt. This amount can be varied, depending upon the kind of the compound used, the kind of organic silver salt, the kind of catalytic amount of silver halide, the kind of reducing agent, the treating temperature, etc. If the amount of the component (e) exceeds the above described range, the degree of coloration of light sensitive layer increases very often, which is disadvantageous in some uses. However, when the material is applied to such uses where coloration is no problem or when compounds of a less degree of coloration are used as the component (e), the amount of the component (e) used can exceed this range.

Suitable organic silver salt, component (a), which can be used in the present invention include, for example, silver salts of organic compounds containing imino, mercapto or carboxyl groups.

Representative examples of these organic silver salts are silver benzotriazole, silver saccharin, silver phthaladinone, the silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, the silver salt of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, the silver salt of 2-(S-ethylthioglycolamido)-benzothiazole, silver caprate, silver laurate, silver myristate, silver palmitate, silver stearate, silver behenate, silver adipate, silver sebacate, etc., as disclosed in U.S. Pat. Nos. 3,457,075 and 3,635,719. Preferably silver salts of organic carboxylic acids and silver benzotriazole are used.

The component (b) of the present invention is (1) a compound which reacts with the silver salt of the component (a) to form a silver halide, or is (2) a silver halide. Representative examples of the former (1) are inorganic compounds of the formula MXn; where M represents a hydrogen atom, an ammonium group or a metal atom (such as a strontium, cadmium, zinc, tin, chromium, sodium, barium, iron, cesium, lanthanum, copper, calcium, nickel, magnesium, potassium, aluminum, antimony, gold, cobalt, mercury, lead, beryllium, lithium, manganese, gallium, indium, rhodium, ruthenium, palladium, iridium, platinum, thallium, bismuth, etc. atom), X represents a halogen atom (such as a chlorine, bromine, or iodine atom), and *n* is 1 when M is a hydrogen atom or an ammonium group, but *n* is the valence of the metal, when M is a metal atom.

In addition, organic halogen compounds such as triphenylmethyl chloride, triphenylmethyl bromide, 2-bromo-2-methylpropane, 2-bromobutyric acid, 2-bromoethanol, benzophenone dichloride, iodoform, bromoform, carbon tetrachloride, etc. are also included in the scope of the compound (1). The silver halide of the latter (2) includes silver chloride, silver bromide, silver iodobromide, silver iodobromochloride, silver bromochloride and silver iodide.

The photosensitive silver halide can be in any form of crude particles and fine particles, and in particular, an emulsion of extremely fine particles is especially useful. A suitable particle size ranges from about 0.003 μ to 0.2 μ, preferably 0.006 μ to 0.1 μ.

An emulsion containing the photosensitive silver halide can be prepared according to any conventional methods known in the field of photography. For example, there may be mentioned emulsions by the single-jet process, emulsions by the double-jet process, for example Lippmann emulsions, ammonia process emulsions, thiocyanate or thioether digested emulsions; for example, emulsions as described in U.S. Pat. Nos. 2,222,264 and 3,320,069 and 3,271,157.

The silver halide used in this invention can be sensitized using conventional chemical sensitizers which are generally used for silver halide emulsions, for example, a reducing agent, a sulfur or selenium compound, a gold, platinum or palladium compound or a mixture thereof. Suitable methods for sensitization are described, for example, in U.S. Pat. Nos. 2,623,499; 2,399,083; 3,297,447 and 3,297,446.

The compound of the above described component (b) can be used alone or in the form of a mixture of two or more compounds. The amount of the component (b) which can be added is suitably in the range of about 0.001 to 0.5 mole, preferably 0.01 to 0.3 mole, per 1 mole of the organic silver salt. If the amount of the component (b) is less than this range, the sensitivity of the material is reduced, but on the contrary, if the amount thereof exceeds this range, the existence of too large an amount of this component (b) causes a disadvantageous phenomenon in that when the material is left under room light after the heat development thereof, the non-image part gradually becomes blackened, resulting in a decrease in the contrast between the non-image part and other image part.

The reducing agent of the component (c) of the present invention must be one suitable for the reduction of the organic silver salt to form silver images, when heated in the presence of the exposed silver halide as a catalyst.

A suitable reducing agent is determined in accordance with the combination of organic silver salt used, and for example, substituted phenols, substituted or unsubstituted bisphenols, substituted or unsubstituted naphthols, di- or poly-hydroxy benzenes, di- or polyhydroxy napthalenes, hydroquinone monoethers, ascorbic acid or derivatives thereof, 3-pyrazolidones, pyrazol-5-ones, reducing saccharides, kojic acid, hinokitiol, etc. are suitable for use.

Representative examples of these compounds are exemplified in the following:

Hydroquinone, chlorohydroquinone, bromohydroquinone, methylhydroquinone, phenylhydroquinone, hydroquinone-monosulfonate, t-octylhydroquinone, t-butylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, p-methoxyphenol, p-ethoxyphenol, hydroquinonemonobenzylether, catechol, pyrogallol, resorcin, p-aminophenol, o-aminophenol, N-methyl-p-aminophenol, 2-methoxy-4-aminophenol, 2,4-diaminophenol, 2-β-hydroxyethyl-4-aminophenol, p-t-butylphenol, p-t-amylphenol, p-cresol, 2,6-di-t-butyl-p-cresol, p-acetophenol, p-phenylphenol, o-phenylphenol, 1,4-dimethoxyphenol, 3,4-xylenol, 2,4-xylenol, 2,6-dimethoxyphenol, 1-amino-2-naphthol-6-sodium sulfonate, 1-naphthylamine-7-sulfonic acid, 1-hydroxy-4-methoxy-naphthalene, 1-hydroxy-4-ethoxy-naphthalene, 1,4-dihydroxynaphthalene, 1,3-dihydroxynaphthalene, 1-hydroxy-4-aminonaphthalene. 1,5-dihydroxynaphthalene, 1-hydroxy-2-phenyl-4-methoxynaphthalene, 1-hydroxy-2-methyl-4-methoxynaphthalene, α-naphthol, β-naphthol, 1,1'-dihydroxy-2,2'-binaphthyl, 4,4'-dimethoxy-1,1'-dihydroxy-2,2'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl,6,6'dinitro-2,2'-dihydroxy-1,1'-binaphthyl, bis(2-hydroxy-1-naphthyl)-methane, bisphenol A, 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 2,4,4-trimethylpenthyl-bis-(2-hydroxy-3,5-dimethylphenyl)-methane, bis(2-hydroxy-3-t-butyl-5-methylphenyl)-methane, bis(2-hydroxy-3,5-di-t-butylphenyl)methane, 4,4'-methlenebis(3-methyl-5-t-butylphenol), 4,4'-methylenebis(2,6-di-t-butylphenol), 2,2'-methylenebis(2-t-butyl-4-ethylphenol), 2,6-dimethylenebis(2-hydroxy-3-t-butyl-5-methyl-benzyl)-4-methylphenol, 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxy-biphenyl, l-ascorbic acid, l-ascorbic acid monoester, l-ascorbic acid diester, p-oxyphenylglycine, N,N-diethyl-p-phenylenediamine, furoin, benzoin, dihydroxyacetone, glycerinaldehyde, rhodizonic acid-tetrahydroxyquinone, methyl gallate, propyl gallate, hydroxytetronic acid, N,N-di(2-ethoxyethyl)hydroxylamine, glucose, lactose, 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, bis(3-methyl-4-hydroxy-5-t-butylphenyl)-sulfide, 3,5-di-t-butyl-4-hydroxybenzyldimethylamine, α,α'-(3,5-di-t-butyl-4-hydroxyphenyl)-dimethylether, etc. These reducing agents can be used as a mixture of two or more of them, if desired.

A suitable reducing agent is selected in combination with the organic silver salt used. For example, higher fatty acid silver salts such as silver behenate are relatively difficultly reduced, and therefore relatively strong reducing agents, for example, bisphenols such as 4,4'-methylenebis(3-methyl-5-t-butylphenol) are suitable therefor. On the other hand, relatively weak reducing agents, for example, substituted phenols such as p-phenylphenol, are suitable for silver salts which are relatively easily reduced, such as silver laurate. In addition, strong reducing agents such as ascorbic acid type reducing agents are suitable for silver salts which are extremely difficultly reduced, such as silver benzotriazole.

The amount of reducing agent to be used in this invention as described above can be varied depending upon the organic silver salt used and the kind of reducing agent used, and therefore, the amount cannot be set forth unequivocally, but in general, a suitable amount ranges from about 0.1 to 5 moles, preferably 0.3 to 2 moles, per 1 mole of organic silver salt.

As is evident from the above explanation, in the formation of the heat developable photographic materials of the present invention, an appropriate reducing agent can be selected and used in combination with a specific organic silver salt, and therefore it is unnecessary to specifically define the organic silver salt and the reducing agent to be used.

In the present invention, the components (a), (b), (c) and (e) are preferably dispersed in a binder and applied on a support. For example, all of the components (a) (b) (c) (e) can be together dispersed in a binder and applied on a support as one layer, or alternatively, these components (a) (b) (c) (e) can be divided into groups thereof and dispersed separately in the binder and then the respective dispersions are applied on a support as individual layers. As the binder component (d) which can be used, any and every conventional binder which has heretofore been used in this field. In general, hydrophobic binders are preferred, but hydrophilic binders can also be used. These binders are preferably transparent or semi-transparent, and suitable examples are, for example, natural substances, such as gelatin, gelatin derivatives or mixtures thereof with latex type vinyl polymers, cellulose derivatives, and synthetic polymer substances, etc.

Representative examples of these binders are as follows: gelatin, gelatin phthalide, polyacrylamide, polyvinyl butyral, cellulose acetate-butyrate, cellulose acetate-propionate, polymethylmethacrylate, polyvinyl pyrrolidone, polystyrene, ethyl cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymer, vinyl chloride-vinyl acetate copolymer, vinyl acetate-vinyl chloride-malaic acid copolymer, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, cellulose acetate, cellulose propionate, cellulose acetatephthalate, etc. If desired, two or more of these binders can optionally be used in admixture. The amount of the binder is suitably in a ratio (by weight) of 4:1 to 1:4, preferably 3:1 to 1:3, on the basis of the organic silver salt. If the component (a) or (c) is a high molecular substance which has the function of a binder, the use of a binder can be omitted.

With respect to the support which can be used in the present invention, various kinds of substances over a broad range can be used. Representative supports are, for example, cellulose nitrate films, cellulose ester films, poly(vinylacetal) films, polystyrene films, poly(ethylene-terephthalate) films, polycarbonate films, and glass, paper, metal, etc. supports.

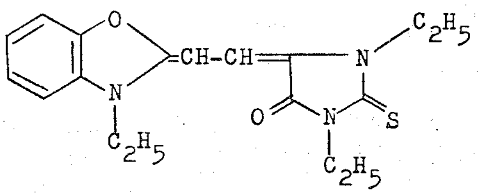
An antistatic layer or a conductive layer can be provided in the heat developable photographic materials of this invention. In addition, an anti-halation substance and an anti-halation dye can also be incorporated therein.

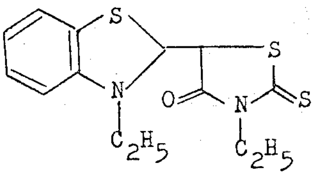
In addition, the heat developable photographic materials of this invention can optionally contain matting agents, such as starch, titanium dioxide, zinc oxide and silica. Further, fluorescent brightening agents such as stilbine, triazine, oxazole and coumarin type fluorescent brightening agents can also be contained therein.

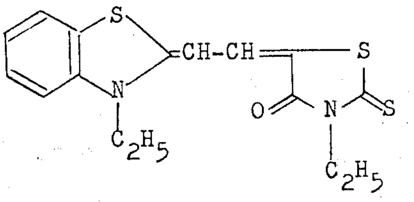
The heat developable photosensitive layer of this invention can be applied on a support using various coating methods, for example, using a dip method, an air-knife method, a curtain coating method as well as an extrusion coating method with a hopper as described in U.S. Pat. No. 2,681,294. If desired, two or more layers can simultaneously be applied. A suitable coating amount ranges from about 0.1 to 3 g (as silver) per m^2, preferably 0.3 to 2 g (as silver) per m^2, of the support.

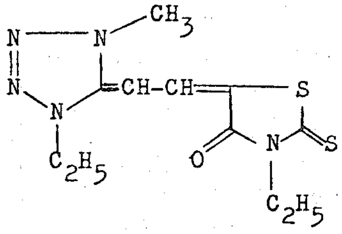
Some kinds of optical sensitizing dyes which have heretofore been used for silver halide emulsions can advantageously be used in the heat developable photographic materials of the present invention for imparting additional sensitivity thereto. For example, cyanine dyes and merocyanine dyes as the optical sensitizing dye as disclosed in U.S. Pat. Nos. 3,457,075 and 3,761,279 can be used in the present invention.

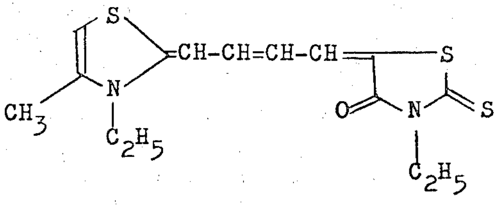
Examples of suitable merocyanine dyes are as follows:



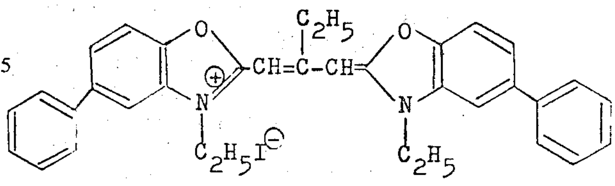


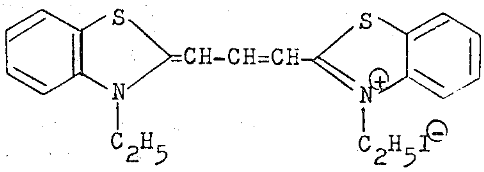


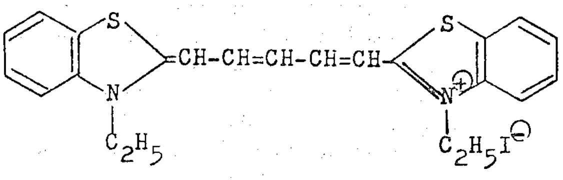


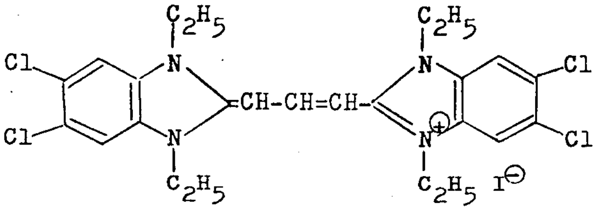


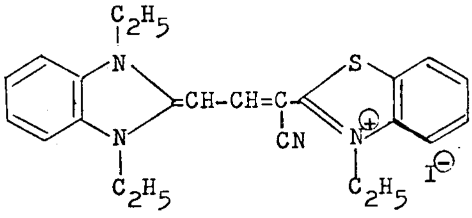
Examples of the suitable cyanine dyes are as follows:











These sensitizing dyes are preferably added to photographic materials in the form of a solution or dispersion dissolved or dispersed in an organic solvent. In this invention, the use of the optical sensitizing dye together with the sensitizer component (e) of this invention causes an increase in the sensitivity of the resulting heat developable photographic material. The content of the optical sensitizing dye in the photographic material of this invention is about 10^{-6} to 10^{-2} mole per 1 mole of the organic silver salt component (a). If the sensitizer of the present invention is effective also as optical sensitizer, the optical sensitizing dye need not necessarily be used.

In addition, an over-coating polymer layer can optionally be provided on the photosensitive layer of the heat developable photographic material of this invention, for the purpose of increasing the transparency of the photosensitive layer, increasing the density of the formed image and improving the storability of the material which exists originally (that is, the ability to maintain the original photographic properties, or those immediately after the preparation of the photographic material, even after the storage thereof). The thickness of this over-coating polymer layer film is suitably 1 to 20 μ.

Suitable polymers are, for example, as follows: polyvinyl chloride, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, polyvinyl butyral, polystyrene, polymethylmethacrylate, polyurethane rubber, xylene resin, benzylcellulose, ethyl cellulose, cellulose acetate-butyrate, cellulose acetate, polyvinylidene chloride, chlorinated polypropylene, polyvinyl pyrrolidone, cellulose propionate, polyvinyl formal, cellulose acetate-phthalate, polycarbonate, cellulose acetate-propionate, etc.

The above described heat developable photographic materials can be developed merely by heating the same, after imagewise exposure to a light source such as a xenon lamp, tungsten lamp, mercury lamp, etc. The temperature used in the heating is suitably in the range of 100° to 160°C, more preferably 110° to 140°C. A higher temperature or a lower temperature can be selected within the above described range, by prolonging or reducing the heating time. The time for development is in general about 1 to 60 seconds.

Various means can be employed for the heat development of the photographic materials of this invention, for example, the photographic material can be brought into contact with a simple hot plate or the like, or can be brought into contact with a heated drum, or as the case may be, can also be passed through a heated space. In addition, high frequency induction heating or laser beam heating can also be utilized.

Now, the present invention will be explained in greater detail by reference to the following Examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

EXAMPLE 1

3.4 g of behenic acid were dissolved in 100 ml of toluene at 60°C and the resulting solution was adjusted to 60°C. While stirring with a stirrer, 100 ml of a diluted nitric acid aqueous solution (pH = 2.0 at 25°C) were added and mixed therewith. The resulting mixture solution was kept at 60°C, and while continuously stirring with a stirrer, 100 ml of an aqueous solution containing silver-ammonium complex were added thereto. (The complex solution was prepared as follows: Aqueous ammonia was added to about 80 ml of an aqueous solution containing 1.7 g of silver nitrate to form a silver-ammonium complex, and water was added thereto to make a total of 100 ml of aqueous solution.) Thus, a dispersion containing fine crystals of silver behenate was obtained. This dispersion was left at room temperature (about 20 to 30°C) for 20 minutes, whereby an aqueous layer and a toluene layer separated from each other.

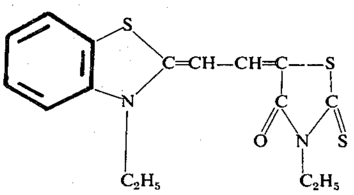
The aqueous layer was first removed, and 400 ml of water were added anew to the remaining toluene layer, which was then washed therewith according to a decantation method. This operation was repeated three times, and then 400 ml of toluene were added to separate the silver behenate by centrifuging. 4 g of silver behenate were obtained in the form of spindle-shaped crystals (long side: about 1 μ; short side: about 0.05 μ).

2.5 g of the silver behenate obtained were added to 20 ml of an iospropyl alcohol solution containing 2 g of polyvinyl butyral and subjected to ball-milling for 1 hour to form a polymer dispersion. To 20 ml of the thus formed silver salt-polymer dispersion were added the following components to prepare a heat developing-out photographic composition, which was then applied to a polyethylene terephthalate film support in an amount of 1.5 g (silver content)/m^2 (support) to produce heat developable Photographic Material (A).

Ammonium Bromide (2.5 wt% methanol solution)	1 ml
Compound (3) (0.025 wt% cellosolve solution)	5 ml
2,2'-Methylenebis(6-t-butyl-4-methylphenol) (2.5 wt% methyl cellosolve solution)	3 ml
Phthaladinone (2.5 wt% methyl cellosolve solution)	1 ml

Separate from this, two other kinds of heat developable photographic materials (B) and (C) were prepared in a similar manner for comparison: the former (B) not containing the sensitizer of the present invention of the above Compound (3), and the latter (C) containing, as a sensitizing dye, the same amount of the following merocyanine dye in place of Compound (3).

Merocyanine Dye used in Material (C):



On the photosensitive layer of each of these photographic materials (A) - (C) was further over-coated a 15 wt% tetrahydrofuran of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt% of vinyl chloride and 5 wt% of vinyl acetate), to form an overcoating film of a thickness of 10 μ (after drying).

These three kinds of photographic materials were exposed to a tungsten light source in an exposure amount of 240,000 lux. sec through an optical wedge, and thereafter heated for 10 seconds at 120°C for development. In each of the thus developed materials, the photographic transmission density thereof was measured. The reciprocal of the amount of exposure required for imparting a higher photographic transmission density than fog (transmission density occurring upon heating of the non-exposed part) by 0.1 was selected for estimation of the sensitivity. The relative sensitivity of the Material (B) was set equal to 100 and other data are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	23,000	100	600

From the above results, it can be seen that the sensitizer of the present invention has an extremely high sensitizing effect, in comparison with the material (A) with the other material (B) or (C).

EXAMPLE 2

In this Example, the same amount of the merocyanine dye of Example 1 was used together with Compound (3), in place of the latter Compound (3) only, and the others were the same as in Example 1.

The results obtained are shown in the following Table. It can be seen therefrom that the sensitizer of the present invention displays a very excellent sensitizing effect due to the joint use with the merocyanine dye.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	33,000	100	600

EXAMPLE 3

In this Example, the same amount of the above described Compound (6) was used in place of Compound (3), and the others were the same as in Example 1.

The results obtained are shown in the following Table. The effect of the present sensitizer is similar to that obtained in Example 1.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	8,000	100	600

EXAMPLE 4

The same amount of the above described Compound (1) was used in place of Compound (3), and the others were the same as in Example 1.

The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	21,000	100	600

The effect of the present sensitizer is similar to that obtained in Example 1.

EXAMPLE 5

A solution of 11 g of lauric acid dissolved in 100 ml of isoamyl acetate was kept at 5°C, and, while stirring, 100 ml of a diluted nitric acid aqueous solution (pH=2.0 at 25°C) were added thereto and admixed, and then while further continuously stirring, 50 ml of a silver nitrate-ammonium complex aqueous solution (cooled to 0°C) containing 8.5 g of silver nitrate were added thereto over course of 1 minute thereby to react the lauric acid and the silver ion.

Spindle-shaped crystals of silver laurate were obtained (long side: about 0.8 μ; short side: about 0.04 μ). After the thus prepared silver salt was washed with water and then with methanol, 3.0 g of polyvinyl butyral and 20 ml of isopropyl alcohol (per 2.7 g of silver laurate) were added thereto to disperse the silver salt in a ball-mill, whereby a silver salt-polymer dispersion was prepared.

To 20 ml of this silver salt-polymer dispersion were added the following components to prepare a heat developing-out photographic composition, which was then applied to a polyethylene terephthalate film support in an amount of 1.7 g (silver content)m^2 (support) to produce a heat developable photographic material (A).

1,3-Dibromo-5,5-dimethylhydantoin (2.5 wt% methyl cellosolve solution)	1 ml
Ammonium Bromide (2.5 wt% methanol solution)	1 ml
Compound (7) (0.025 wt% methyl cellosolve solution)	5 ml
p-Phenylphenol (70 wt% methyl cellosolve solution)	3 ml
Phthaladinone (2.5 wt% methyl cellosolve solution)	1 ml
Anhydrous Tetrachlorophthalic Acid (0.6 wt% methanol solution)	1 ml

Separately from this, two other kinds of heat developable photographic materials (B) and (C) were prepared in a similar manner for comparison: the former (B) not containing the sensitizer of the present invention, the above Compound (7), and the latter (C) containing, as a sensitizing dye, the same amount of the merocyanine dye (of Example 1) in place of Compound (7).

On the photosensitive layer of each of the thus produced photographic materials (A) to (C) was further over-coated a 15 wt% tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt% of vinyl chloride and 5 wt% of vinyl acetate), to form an over-coating film of a thickness of 10 μ (after drying).

These three kinds of photographic materials (A) to (C) were exposed to a tungsten light source in an exposure amount of 200,000 lux.sec through an optical wedge, and thereafter heated for 7 seconds at 120°C for development. In each case, the photographic transmission density was measured and the relative sensitivity was calculated in a manner similar Example 1. The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	18,000	100	500

From the above results, it is understood that the sensitizer of this invention displays an extremely excellent sensitizing effect.

EXAMPLE 6

Using the same process of Example 5, the same amount of the above described Compound (21) was used in place of Compound (7). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	15,000	100	500

It is noted that Compound (21) has an excellent sensitizing effect similar to Compound (7) of Example 5.

EXAMPLE 7

Using the process of Example 5, the same amount of the above described Compound (15) was used in place of Compound (7). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	9,700	100	500

Compound (15) also is effective as a sensitizer, similar to Compound (7) of Example 5.

EXAMPLE 8

6 g of benzotriazole were dissolved in 100 ml of isoamyl acetate at 50°C and then cooled and adjusted to −15°C. While stirring with a stirring with a stirrer, a solution of 8.5 g of silver nitrate dissolved in 100 ml of a diluted nitric acid aqueous solution (pH=2.0 at 25°C), which was adjusted to 3°C, was added thereto. Thus, a dispersion containing fine crystals of silver benzotriazole was prepared. The resulting dispersion was left at room temperature for 20 minutes, whereupon an aqueous phase and an isoamyl acetate phase separated from each other. The aqueous phase was first removed, and 400 ml of water were added anew to the remaining phase to wash the same by a decantation method. This operation was repeated three times, and then 400 ml of methanol were added to separate silver benzotriazole by centrifuging. Thus, 8 g of silver benzotriazole were obtained. The particles of the silver benzotriazole were of a nearly spherical form, having a particle size of about 1 μ (diameter) 2.5 g of the thus formed silver benzotriazole were added to 40 ml of an isopropyl alcohol solution containing 4 g of polyvinyl butyral and subjected to ball-milling for 4 hours to disperse the same, whereby a silver salt-polymer dispersion was prepared. To 40 ml of the resulting silver salt-polymer dispersion were added the following components to form a heat developable photographic composition, which was then applied on a polyethylene terephthalate film support in an amount of 1.2 g (coated silver content)m^2 (support) to produce a heat developing-out photographic material (A).

Ammonium Iodide (8.5 wt% methanol solution)	1 ml
Solution Containing 2 g of Ascorbic Acid Monopalmitate and 2 g of Ascorbic Acid Dipalmitate in 10 ml of Methyl Cellosolve	10 ml
Compound (5) (0.2 wt% methyl cellosolve solution)	1 ml
N-Ethyl-N'-dodecylurea (2.5 wt% methyl cellosolve solution)	2 ml

Separately from this, two other kinds of heat developable photographic materials (B) and (C) were prepared in a similar manner for comparison; the former (B) not containing the sensitizer of the present invention, the above Compound (5), and the latter (C) containing, as a sensitizing dye, the same amount of the merocyanine dye (of Example 1) in place of Compound (5).

On the photosensitive layer of each of the thus produced photographic materials (A) to (C) was further over-coated a 15 wt% tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt% of vinyl chloride and 5 wt% of vinyl acetate), to form an over-coating film of a thickness of 8 μ (after drying).

Small pieces of these three kinds of photographic materials (A) to (C) were exposed to a tungsten light source in an exposure amount of 1,200,000 lux.sec through an optical wedge, and thereafter heated for 30 seconds at 130°C for development. In each case, the photographic transmission density was measured and the relative sensitivity was calculated in a manner similar to Example 1. The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	6,500	100	200

From the above results, it can be seen that the sensitizer of this invention displays an extremely excellent sensitizing effect.

EXAMPLE 9

Using the same process of Example 8, the same amount of the above described Compound (22) was used in place of Compound (5). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	5,300	100	200

It can be seen that Compound (22) has an excellent sensitizing effect similar to Compound (5) of Example 8.

EXAMPLE 10

Using the same process of Example 8, the same amount of the above described Compound (6) was used in place of Compound (5). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	4,800	100	200

Compound (6) also is effective as a sensitizer, similar to Compound (5) of Example 8.

COMPARATIVE EXAMPLE

Using the same process of Example 5, the same amount of Compound (7) was used in place of Compound (3).

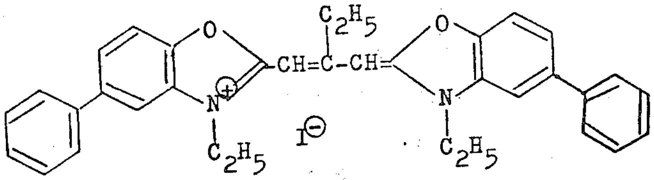
The resulting photographic material was exposed to light of 200,000 CMS and heated at 120°C for 17 seconds to obtain an image (Dmax = 1.6; fog = 0.2).

In the same manner, using the same process of Example 5, the same amount of Erythrocin is used in place of Compound (7).

The resulting photographic material was exposed to light of 200,000 CMS and heated at 120°C for 17 seconds to obtain an image (Dmax = 0.8; fog = 0.4).

EXAMPLE 11

Using the same process of Example 1, the same amount of the following cyanine dye was used together with Compound (3), in place of Compound (3) only.



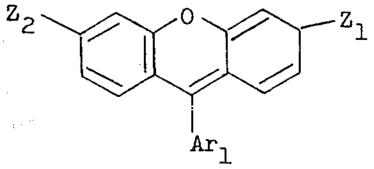
The results obtained are shown in the following Table. It can be seen that the present sensitizer, Compound (3), displays a more excellent sensitizing effect due to joint use with the cyanine dye.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	29,000	100	600

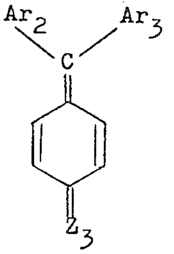
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

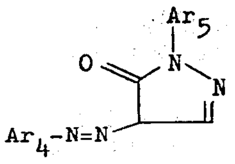
1. A sensitized heat developable photographic material comprising a support having thereon at least one photographic layer containing the following components:
   a. an organic silver salt,
   b. a catalytic amount of a photosensitive silver halide or a compound which reacts with said organic silver salt (a) to produce a photosensitive silver halide,
   c. a reducing agent,
   d. a binder, and
   e. at least one compound of the following formulae:



(I)

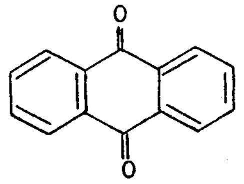


(II)



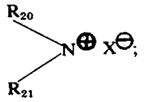
(III)

and

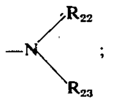


(IV)

wherein Z_1 and Z_3 each represents —O or



Z_2 represents —OM or



Ar_1, Ar_2, Ar_3, Ar_4 and Ar_5 each represents an unsubstituted or substituted aryl group;

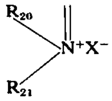
$X^{\ominus}$ represents an anion; and

R_{20}, R_{21}, R_{22} and R_{23} each represents an unsubstituted or substituted alkyl group or an unsubstituted or substituted aryl group; with the proviso that when Z_1 is =O, Z_2 is —OM, and Ar_1 does not contain a halogen substituent, and the nuclei in the formula (I) contain two halogen atoms;

Ar_1 contains at least one of SO_3M and COOM as a substituent; at least one of Ar_2 and Ar_3, and at least one of Ar_4 and Ar_5 each contains at least one of SO_3M and COOM as a substituent;

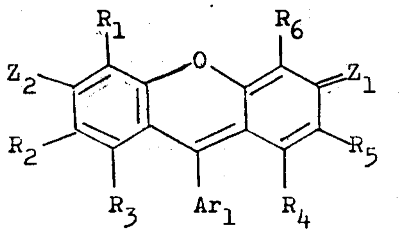
the formula (IV) contains at least one of SO_3M and COOM as a substituent in the nuclei thereof or in the substituent(s) on the nuclei thereof;

M represents a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, or an NH_4 group, and each nucleus of the formulae (I) through (IV) can further contain additional substituent(s) other than the above defined substituents, and the radical

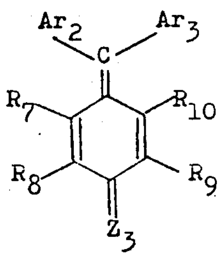


can be in the form of an inner salt.

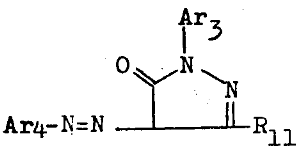
2. The photographic material as claimed in claim 1, wherein said component (e) is selected from the group consisting of compounds having the following formula:



(I')

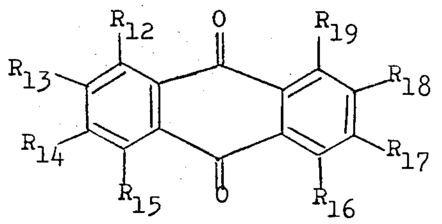


(II')



(III')

and



(IV')

wherein R_1 through R_9, R_{13}, R_{14}, R_{17} and R_{18} each represents a member selected from the group consisting of a hydrogen atom, an alkyl group, an aryl group, a halogen atom, a nitro group, a hydroxyl group, an SO_3M group, a COOM group, an alkoxy group, an acyl group and an amino group; with the proviso that when Z_1 is =O, Z_2 is —OM and Ar_1 does not contain a halogen substituent, with two of these R_1 through R_6 being halogen atoms; R_{10} represents a hydrogen atom on a methyl group.

R_{11} represents a hydrogen atom, an alkyl group or a COOM group; R_{12}, R_{15}, R_{16} and R_{19} each represents a member selected from the group consisting of a hydrogen atom, an amino group, an alkylamino group, an arylamino group, an alkyl group, a halogen atom, a hydroxyl group, an SO_3M group and a COOM group, and at least one of R_{12} through R_{19} is a radical having a SO_3M group and/or a COOM group, and Z_1, Z_2, Z_3, Ar_1, Ar_2, Ar_3, Ar_4, Ar_5 and M are as defined in claim **1**.

3. The photographic material as claimed in claim **1**, wherein Ar_1, Ar_2, Ar_3, Ar_4 and Ar_5 each represents an unsubstituted or substituted phenyl group, or an unsubstituted or substituted α- or β-naphthyl group.

4. The photographic material as claimed in claim **3**, wherein said aryl group is substituted with an alkyl group, a halogen atom, a hydroxy group, an SO_3M group, a COOM group, an aryl group, a nitro group, an amino group, an acyl group or an alkoxy group.

5. The photographic material as claimed in claim **1**, wherein said alkali metal is Li, Na, K or Rb.

6. The photographic material as claimed in claim **1**, wherein said alkaline earth metal is Ca, Mg or Ba.

7. The photographic material as claimed in claim **1**, wherein said alkyl group, alkoxy group, acyl group and alkylamino group represented by Ar_1 through Ar_5 and R_1 through R_{19} have 1 to 8 carbon atoms.

8. The photographic material as claimed in claim **1**, wherein the substituents of said aryl group and R_1 through R_{19} are a methyl group, an ethyl group, an isopropyl group, a t-butyl group, an ethoxy group, an acetyl group or a dimethylamino group.

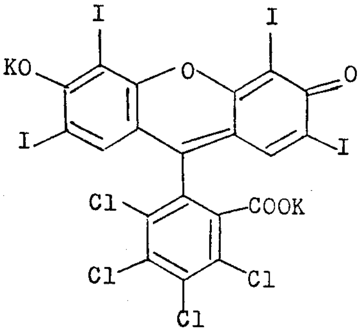
9. The photographic material as claimed in claim **2**, wherein R_{20} through R_{23} each represents an alkyl group having 1 to 8 carbon atoms.

10. The photographic material as claimed in claim **9**, wherein said alkyl group is substituted with a phenyl group or a sodium sulfophenyl group.

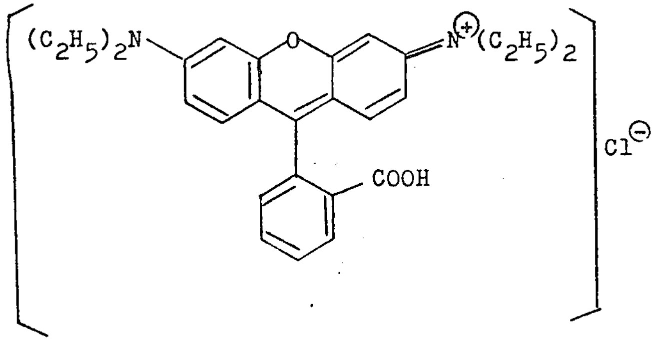
11. The photographic material as claimed in claim **1**, wherein said aryl group represented by R_{20} through R_{23} is substituted with a phenyl group, a sodium sulfophenyl group or a tolyl group.

12. The photographic material as claimed in claim **1**, wherein said component (e) is selected from the group consisting of the following compounds

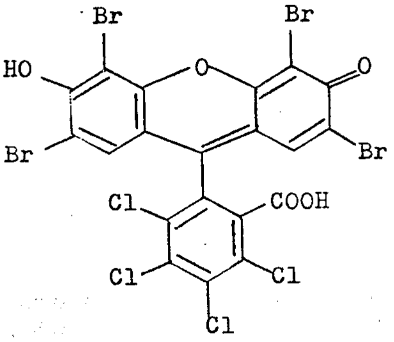
(1)



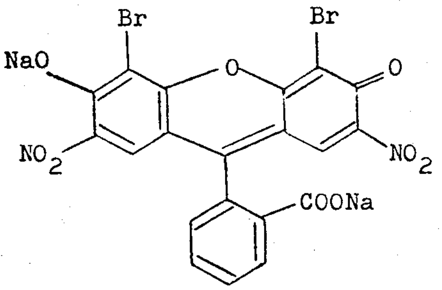
(2)



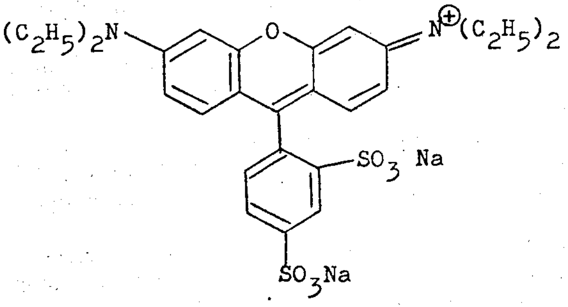
(3)



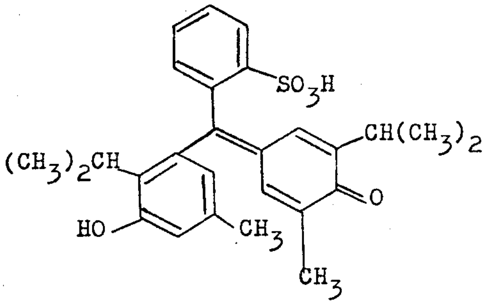
(4)



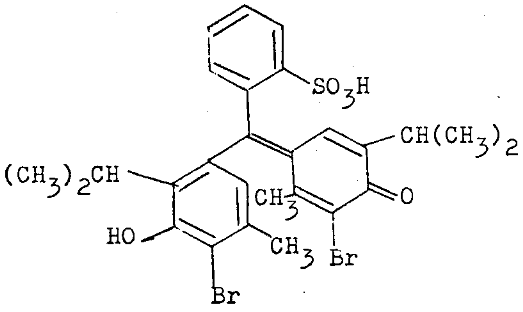
(5)



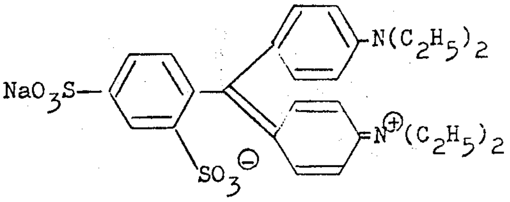
(6)



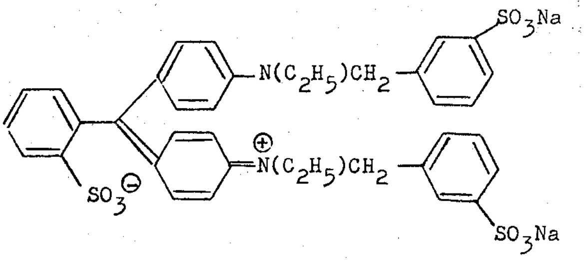
(7)



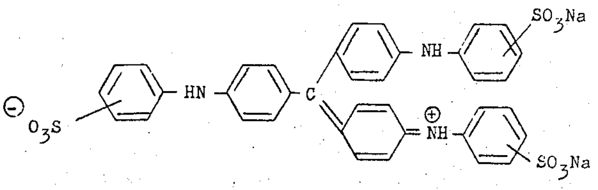
(8)



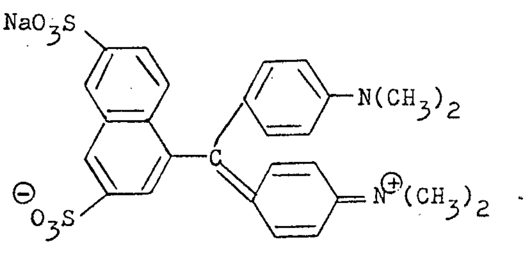
(9)



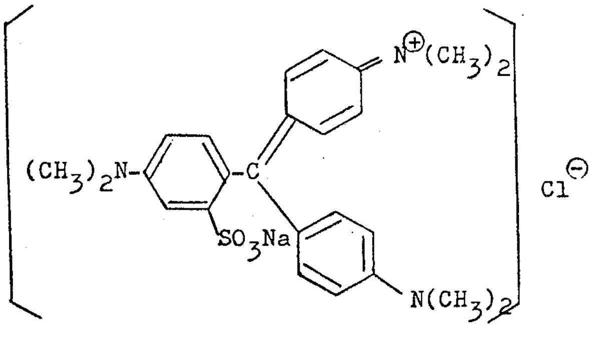
(10)



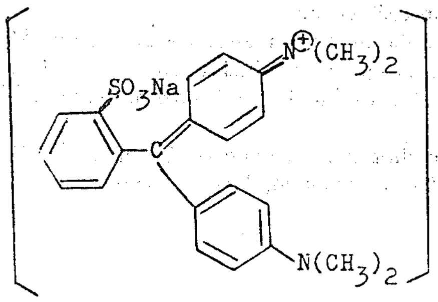
(11)



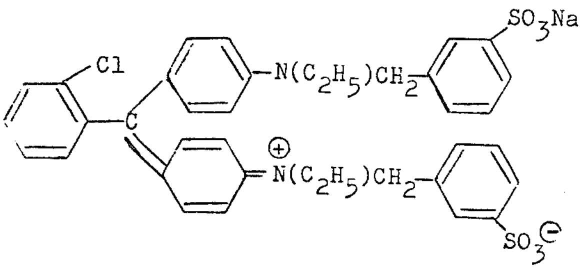
(12)



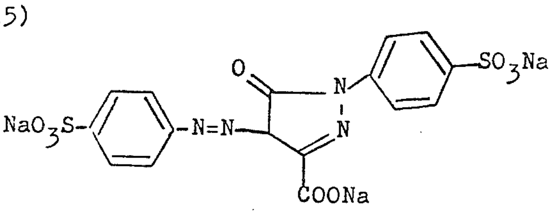
(13)



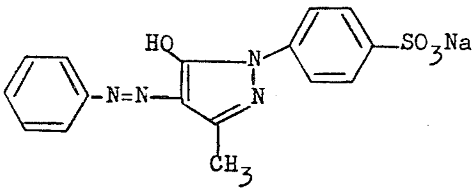
(14)



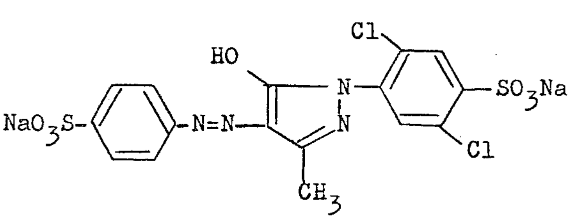
(15)



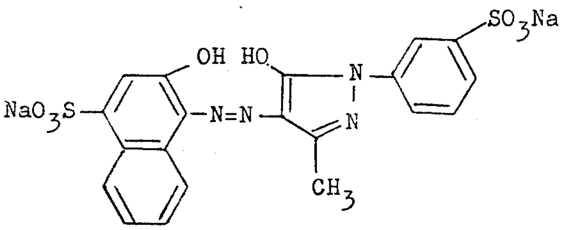
(16)



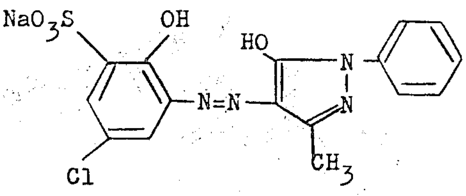
(17)



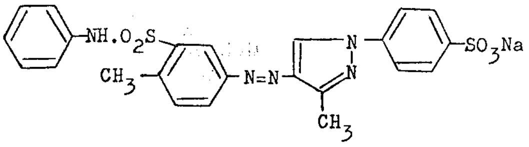
(18)



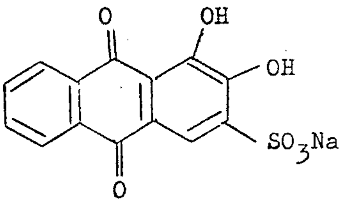
(19)



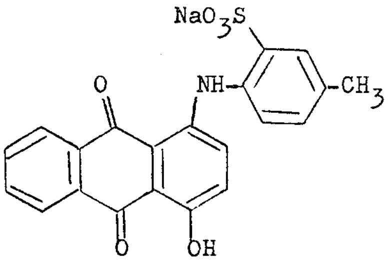
(20)



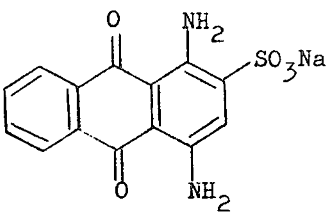
(21)



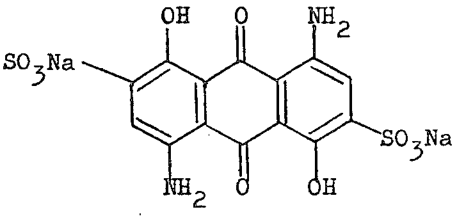
(22)



(23)

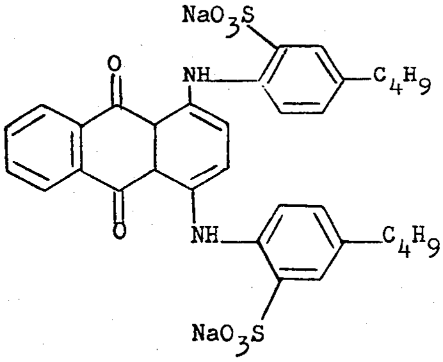


(24)



and

(25)



13. The photographic material as claimed in claim **1,** wherein said component (e) is present in an amount ranging from about 10^{-6} to 10^{-2} mole per 1 mole of said organic silver salt.

14. The photographic material as claimed in claim **1,** including an optical sensitizing dye, in an amount of about 10^{-6} to 10^{-2} mole per 1 mole of said organic silver salt.

15. The photographic material as claimed in claim **1,** including an over-coating layer on said photosensitive layer.

* * * * *