

[54] **HEAT DEVELOPABLE PHOTOGRAPHIC MATERIAL CONTAINING AZO DYES AS SENSITIZERS**

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[30] **Foreign Application Priority Data**

Jan. 17, 1973 Japan..... 48-7624

[52] U.S. Cl..... **96/114.1, 96/67, 96/139**

[51] Int. Cl..... **G03c 1/02**

[58] Field of Search 96/114.1, 114.6, 109, 107,
96/108; 117/36.7, 36.8

[56] **References Cited**

UNITED STATES PATENTS

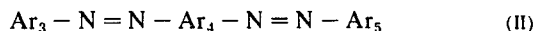
3,457,075	7/1969	Morgan et al.	96/114.1
3,645,739	2/1972	Ohkubo et al.	96/114.1
3,700,457	10/1972	Youngquist	96/114.1
3,770,448	11/1973	Poot et al.	96/114.1

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Zinn & Macpeak

[57] **ABSTRACT**

Heat developable photographic materials 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. as a sensitizer, at least one of the following compounds (I) and (II):



wherein Ar_1 , Ar_2 , Ar_3 and Ar_5 each represents an aryl group and Ar_4 represents an arylene group, with the proviso that at least one of Ar_1 and Ar_3 , and at least one of Ar_3 , Ar_4 and Ar_5 are substituted with $-\text{SO}_3\text{M}$ or $-\text{COOM}$, M being a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, or a $-\text{NH}_4$ group. The sensitizer (e) has a particularly excellent sensitizing effect.

12 Claims, No Drawings

HEAT DEVELOPABLE PHOTOGRAPHIC MATERIAL CONTAINING AZO DYES AS SENSITIZERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

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

2. Description of the Prior Art

A photographic process using silver halides is the process which has heretofore been most widely utilized due to the excellent photographic properties thereof, such as high sensitivity and good gradation over any of the other processes such as an electrophotographic process or a diazo-photographic process. However, silver halide photographic materials used in this process are developed with a developer after image-wise exposure thereof, and then, they are subjected to several after-treatments such as stopping, fixation, washing with water or stabilization so that the developed images are not discolored or deteriorated under normal light or so that the non-developed part (hereunder referred to as "background") is not blackened. Accordingly, these treatments require time and labor. In addition, there are the danger to working personnel due to contact with the chemicals and the difficulties in that the interior of the treating room and the hands and clothes of operators are stained. 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 employed in the present 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 Pat. Publication Nos. 26582/69 and 22185/70, British Pat. No. 1,205,500, and U.S. Pat. Nos. 3,152,904, 3,457,075, 3,635,719, and 3,645,739, etc.

This invention relates to the third approach among the above described three types of methods.

However, sufficient photosensitivity can not as yet be attained in the conventional heat developing-out photographic materials, for example those comprising compositions of a fatty acid silver salt, a reducing agent and a catalytic amount of silver halide.

Regarding conventional techniques for sensitization of conventional heat developing photographic materials, the description, for example, in the above described U.S. Pat. No. 3,457,075 which belongs to the

third method, is that known merocyanine dyes are effective as so-called optical sensitizers for silver halide emulsions. 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 of this invention.

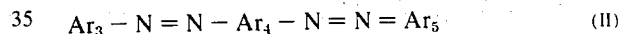
SUMMARY OF THE INVENTION

An object of this invention is to provide heat developable photographic materials having at least one sensitized light-sensitive layer.

The present inventors have conducted various research in an effort to obtain such sensitizers which are effective for heat developable photographic materials, and have at last found that the compounds of formulae (I) (II) as described herein have excellent sensitizing effects for the heat developable photographic materials of this invention.

This invention therefore relates to heat developable photographic materials having at least one layer on a support, which layer contains 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. as a sensitizer, at least one of the following compounds (I) and (II);



wherein Ar_1 , Ar_2 , Ar_3 and Ar_5 each represents an aryl group and Ar_4 represents an arylene group, with the proviso that at least one of Ar_1 and Ar_2 , and at least one of Ar_3 , Ar_4 and Ar_5 are substituted with a $-\text{SO}_3\text{M}$ or $-\text{COOM}$ group with M being a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, or a $-\text{NH}_4$ group.

DETAILED DESCRIPTION OF THE INVENTION

Suitable aryl group represented by Ar_1 , Ar_2 , Ar_3 and Ar_5 in the above formulae includes phenyl, α -naphthyl and β -naphthyl groups, which can be unsubstituted or substituted. Suitable arylene groups represented by Ar_4 includes phenylene, biphenylene and naphthylene groups, which can be unsubstituted or substituted. Suitable substituents of these aryl and arylene groups include alkyl groups (e.g., methyl groups, ethyl groups, t-butyl groups, etc.), halogen atoms (e.g., chloride atoms, bromine atoms, iodine atoms), hydroxyl groups, $-\text{SO}_3\text{M}$ groups, $-\text{COOM}$ groups, aryl groups (e.g., phenyl groups, tolyl groups, xylol groups, etc.), nitro groups, amino groups, alkylamino groups, arylamino groups, acyl groups (e.g., acetyl groups, propionyl groups, etc.), alkoxy groups (e.g., methoxy groups, ethoxy groups, propoxy groups, etc.), arylsulfonyloxy groups, alkylsulfonyloxy groups, etc. as representative examples.

Of these substituents, the alkyl, alkoxy and acyl groups suitably can have 1 to 8 carbon atoms, preferably 1 to 4 carbon atoms.

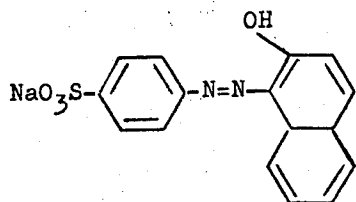
Preferred alkali metals are Li, Na, K, Pb, etc.

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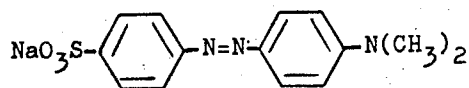
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Preferred alkaline earth metals are Ca, Ba, Mg, etc.
The arylene group bonding can be at any position.
Representative examples of preferred compounds of
this invention are as follows:

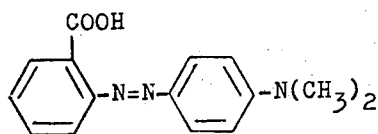
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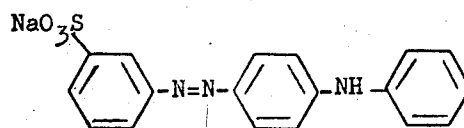


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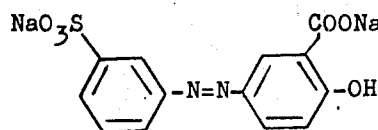
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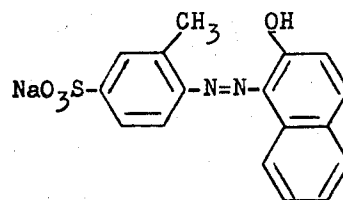
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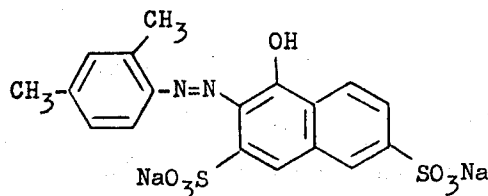
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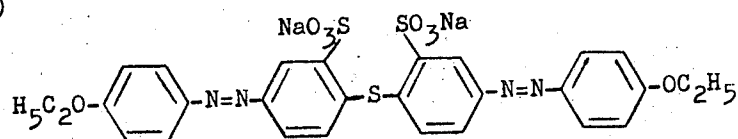


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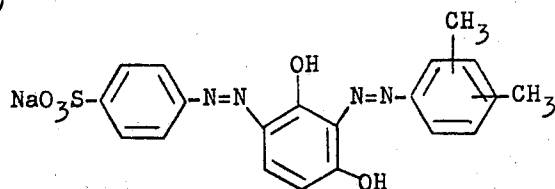
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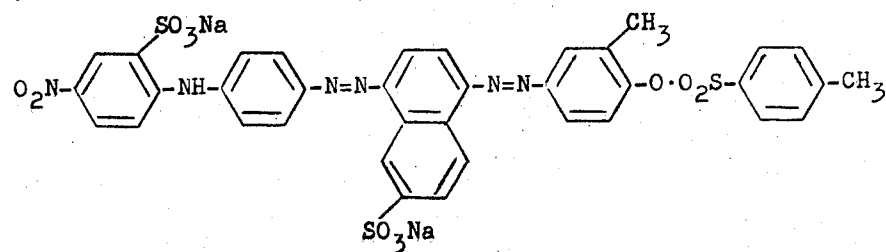
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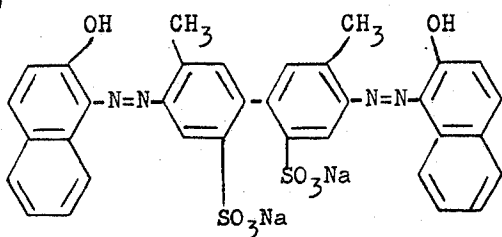
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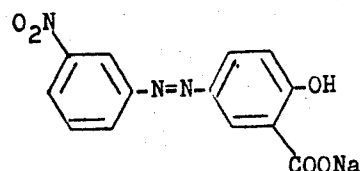
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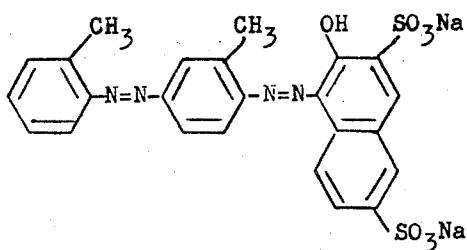
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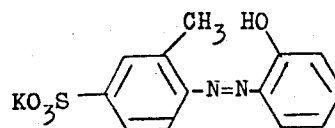
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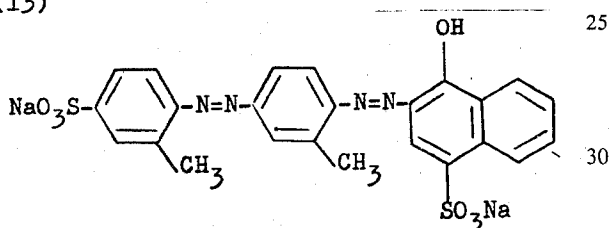
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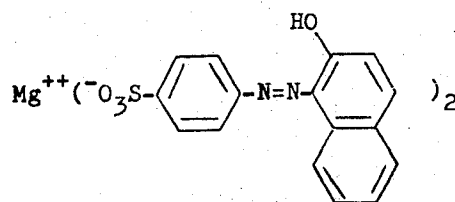
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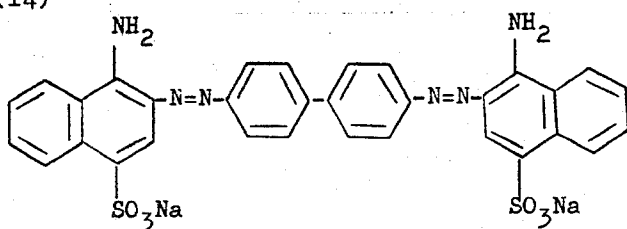
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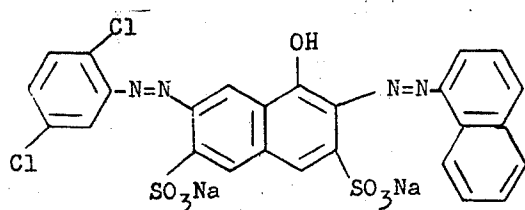
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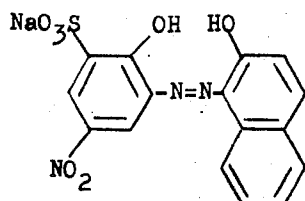
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The amount of the component (e), which is the compound effective as a sensitizer of the present invention, which is added is suitably about 10^{-6} to 10^{-2} mole per 1 mole of the organic silver salt. This amount can be varied, depending upon the kind of the compound used, the kind of the organic silver salt, the kind of the catalytic amount of the silver halide, the kind of the 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 not a problem or when compounds giving rise to less coloration are used as the component (e), the amount of the component (e) which can be used can exceed this range.

The following organic silver salts (component a) are suitable for use in the present invention, for example, the silver salts of organic compounds containing imino, mercapto or carboxyl groups, for example, as disclosed in U.S. Pat. Nos. 3,457,075 and 3,152,904.

Representative examples of these organic silver salts are silver benzotriazole, silver saccharin, silver phthaladione, the silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, the silver salt or 4-hydroxy-6-methyl-1,3,3a,7-tetraindene, the silver salt of 2-(S-ethylthioglycolamido)-benzothiazole, silver caprate, silver laurate, silver myristate, silver palmitate, silver stearate, silver behenate, silver akipate, silver sebacate, etc.

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 compound (1) are inorganic compounds of the formula MX_n , where M represents a hydrogen atom, an ammonium group or a metal atom (such as 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.), X represents a halogen atom (such as chlorine, bromine, iodine), and when M is a hydrogen atom or an ammonium group n is 1, but when M is a metal atom, n is a number corresponding to the valence of the metal.

In addition, organic halogen compounds such as triphenylmethyl chloride, triphenylmethyl bromide, 2-bromo-2-methylpropane, 2-bromobutyric acid, 2-bromoethanol, benzophenone dichloride, iodoform, carbon tetrachloride, etc. can also be included within the scope of compound (1). Suitable silver halides of the latter (2) include silver chloride, silver bromide, silver iodobromide, silver iodobromochloride, silver bromochloride and silver iodide. Suitable examples of components (b) above are disclosed in U.S. Pat. No. 3,457,075.

The photosensitive silver halide can be in any form, such as crude particles or fine particles, and in particular, emulsions of extremely fine particles are especially useful. A suitable particle size can range from about 0.002μ to 2μ preferably 0.006μ to 0.5μ .

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

The silver halide which can be used in this invention can be sensitized with conventional chemical sensitizers which are generally used for silver halide emulsions, for example, with reducing agents, sulfur or selenium compounds, gold, platinum or palladium compounds 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 as a mixture of two or more kinds of compounds. The amount of component (b) which can be added is suitably in the range of about 0.001 to 0.5 mole, preferably 0.01 to 0.2 mol, per 1 mole of organic silver salt. If the amount of the component (b) is lower than this range, the sensitivity of the material is reduced, but on the contrary, if the amount thereof exceeds this range, the presence of too large an

amount of component (b) causes such an unfavorable phenomenon that when the material is left exposed to room light after the heat development thereof, the non-image part gradually blackens, resulting in a decrease in the contrast between the non-image part and the 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 catalyst.

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

Representative examples of these compounds are exemplified in the following:

Hydroquinone, methylhydroquinone, chlorohydroquinone, bromohydroquinone, phenylhydroquinone, hydroquinone-monosulfonate, t-octylhydroquinone, t-butylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, p-methoxyphenol, p-ethoxyphenol, hydroquinone-monobenzyloxy, 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-xyleneol, 2,4-xyleneol, 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-1,4-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-trimethylpentyl-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'-methylenebis(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-methylphenyl)-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-oxophenylglycine, N,N-diethyl-p-phenylenediamine, furon, benzoin, dihydroxyacetone, glycerinaldehyde, rhodizonic acid-tetrahydroxyquinone, methyl gallate, propyl gallate, hydroxy tetronic acid, N,N-di(2-ethoxyethyl)hydroxylamine, glucose, lactose, 1-phenyl-3-pyrazolidone, 4-hydroxymethyl-1-phenyl-3-pyrazolidone, bis(3-methyl-4-hydroxy-5-t-butylphenyl)-sulfide, 3,5-di-t-butyl-4-hydroxybenzyl-

dimethylamine, α, α' -(3,5-di-*t*-butyl-4-hydroxyphenyl)-dimethylether, etc.

These reducing agents can be used in the form of a mixture of two or more of them. A suitable reducing agent is selected in combination with the organic silver salt. For example, the higher fatty acid silver salts such as silver behenate are relatively difficultly reduced, and therefore relatively strong reducing agents, for example, the bisphenols such as 4,4'-methylenebis(3-methyl-5-*t*-butylphenol) are suitable therefor. On the other hand, relatively weak reducing agents, for example, the 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 which is used in this invention as described above will vary depending upon the organic silver salt used and the kind of reducing agent used, and therefore, the amount cannot unequivocally set forth, but in general, the amount suitably ranges from about 0.1 to 5 moles, preferably 0.6 to 2 moles per 1 mole of organic silver salt.

As is evident from the above explanation, in the formation of 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 reducing agent used.

In the present invention, the components (a), (b), (c) and (e) are preferably dispersed in a binder and applied on a support. In this instance, all of the components (a) to (e) are completely dispersed in the binder and applied on a support as one layer, or alternatively, these components (a) to (e) can be separated into groups and dispersed separately in the binder and then the respective dispersions are applied on a support as individual layers. As the binder component (d) any and every conventional binder which has heretofore been used in this field can be used. In general, hydrophobic binders are preferred, but hydrophilic binders can also be used. These binders are preferably transparent or semi-transparent, and suitable binders 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 example of these binders are as follows: gelatin, gelatin phthalide, acrylamide, polyvinyl butyral, cellulose acetate-butyrate, cellulose acetate-propionate, polymethylmethacrylate, polyvinyl pyrrolidone, polystyrene, ethyl-cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadienestyrene copolymers, vinyl chloride-vinyl acetate copolymers, vinyl acetate-vinyl chloride-maleic acid copolymers, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate-phthalate, etc.

The amount of binder is suitably in a ratio (by weight) of about 0.1:1 to 5:1, preferably 0.2:1 to 3:1 on the basis of the amount of the organic silver salt.

If the component (a) or (c) is a high molecular weight substance which has the function of a binder, the use of binder can be omitted.

With respect to the support to be used in the present invention, various kinds of supports in a broad range

can be used. Representative supports are, for example, cellulose nitrate films, cellulose ester films, poly(vinylacetal) films, polystyrene films, poly(ethyleneterephthalate) films, polycarbonate films, and glass, paper, metal, etc. supports a suitable coating amount ranges from 0.1 to 3 g/m², preferably 0.3 to 2 g/m².

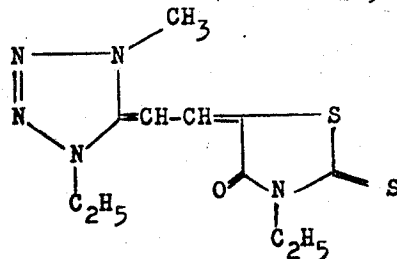
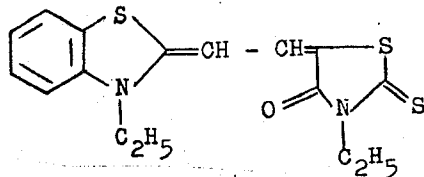
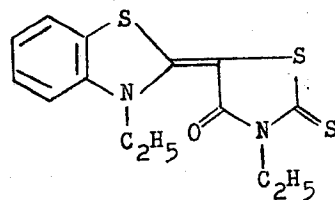
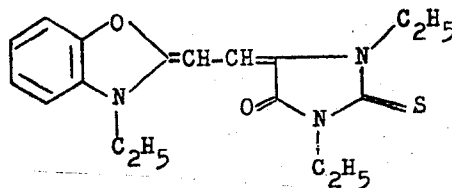
An antistatic layer or a conductive layer can be provided in the heat developing photographic materials of this invention. In addition, an anti-halation material and an anti-halation dye can also be incorporated therein.

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 whitening agents such as stilbene, triazine, oxazole, and coumarin type fluorescent whitening agents can also be contained therein.

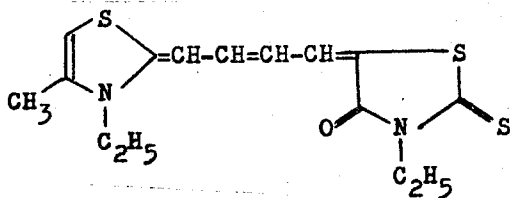
The heat developable photosensitive layer(s) of this invention can be applied to a support using various coating methods, for example, the dip method the air-knife method, the curtain coating method as well as the extrusion coating method with a hopper as described in U.S. Pat. No. 2,681,294. If necessary, two or more layers can be simultaneously applied.

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

Example of suitable merocyanine dyes are as follows:

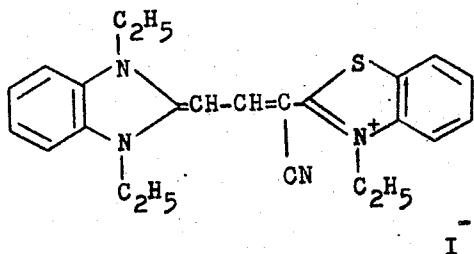
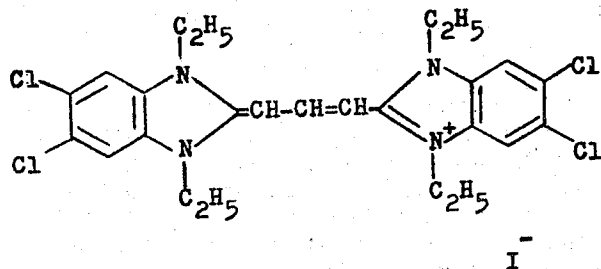
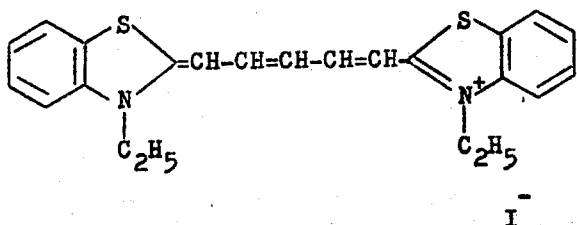
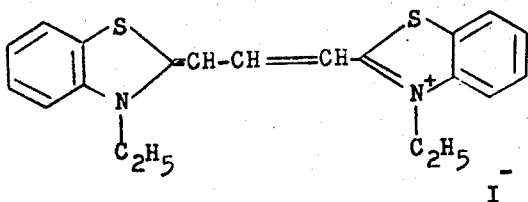
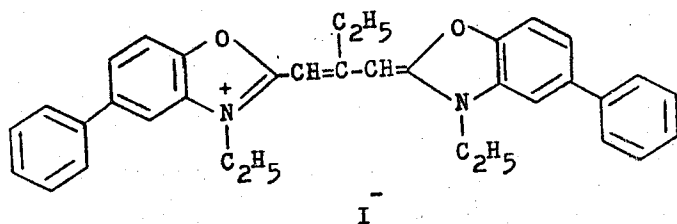


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developable photographic material. The content of the optical sensitizing dye in the photographic material of this invention is about 10^{-6} to 10^{-2} mole per 1 mole of the organic silver salt component (a). If the sensitizer of the present invention is effective also as an optical sensitizer, the optical sensitizing dye need not necessarily be used. In addition, an over-coating polymer layer



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 of sensitivity of the resulting heat

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 image formed and improving the storability of the freshness of said material (that is, the ability to maintain the original photographic properties, or those existing immediately after the preparation of the photographic material, even after storage thereof). The thickness of this over-coating polymer layer film is suitably 1 to 20 μ .

Suitable polymers for this layer are, for example, as follows: polyvinyl chloride, polyvinyl acetate, vinyl chloridevinyl acetate copolymers, polyvinyl butyral, polystyrene, polymethylmethacrylate, polyurethane rubbers, xylene resins, benzylcellulose, ethyl cellulose, cellulose acetate-butyrate, cellulose acetate, polyvinylidene chloride, chlorinated polypropylene, polyvinyl pyrrolidone, cellulose propionate, polyvinyl formal, cellulose acetate-phthalate, polycarbonate, cellulose acetatepropionate, etc.

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

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 zone. 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, an aqueous solution containing a silver-ammonium complex is added thereto. This 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 the total volume of the aqueous solution 100 ml.) Thus, a dispersion containing fine crystals of silver behenate was obtained. This dispersion was left at room temperature (about 20°–30°C) for 20 minutes, whereby an aqueous layer and a toluene layer were separated from each other.

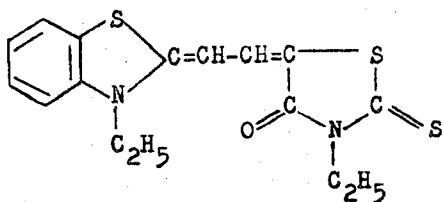
The aqueous layer was first removed, and 400 ml of water were added again to the remaining toluene layer, which was then washed therewith according to the decantation method. This operation was repeated three times, and then 400 ml of toluene were added to separate the silver behenate by centrifuging. 4 g of silver behenate were obtained in the form of spindle-shaped crystals (long side: about 1 μ , short side: about 0.005 μ).

2.5 g of the obtained silver behenate were added to 20 ml of an isopropyl 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 developable photographic composition, which was then applied to a polyethylene terephthalate film support in an amount of 1.5 g (silver content)/m² (support) to produce heat developable photographic material (A).

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

A part from this, two other kinds heat developable photographic materials (B) and (C) are prepared in a similar manner for comparison: the former (B) not containing the sensitizer Compound (3) of the present invention, 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 percent tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt percent of vinyl chloride and 5 wt percent of vinyl acetate), to form an over-coating film of a thickness of 10 μ (after drying).

These three kinds of photographic materials were exposed to a tungsten light source in an amount of exposure of 240,000 luc.sec through an optical wedge, and thereafter heated for 10 seconds at 120°C for develop-

ment. In each of the thus developed materials, the photographic transmission density thereof was measured. A reciprocal of amount of exposure required for imparting a higher photographic transmission density than fog (transmission density occurring upon heat of the non-exposed part) by 0.1 was selected for an estimation of the sensitivity. The relative sensitivity of the material (B) was set at 100 and other data are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	14,000	100	600

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

EXAMPLE 2

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

The results obtained are shown in the following Table. It can be understood 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	21,000	100	600

EXAMPLE 3

In this Example, the same amount of the above described Compound (2) was used in place of Compound (3), and others materials 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 of Example 1.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	12,000	100	600

EXAMPLE 4

The same amount of the above described Compound (15) was used in place of Compound (3), and others materials were the same as in Example 1.

The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	9,300	100	600

The effect of the present sensitizer is similar to that of the 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 containing 8.5 g of silver nitrate were added thereto over the course of 1 minute thereby to react the lauric acid and 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 the silver salt-polymer dispersion were added the following components to prepare a heat developable photographic composition, which was then applied to a polyethylene terephthalate film support in an amount of 1.7 g (silver content)/m² (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 (3) (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

Apart from this, two other kinds 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 (3), and the latter (C) containing, as sensitizing dye, the same amount of the merocyanine dye (of Example 1) in place of Compound (3).

On the photosensitive layer of each of the thus produced photographic materials (A) to (C) was further over-coated a 15 wt percent tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt percent of vinyl chloride and 5 wt percent 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 amount of exposure 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 similar manner to Example 1. The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	18,700	100	500

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

EXAMPLE 6

In the same manner as in Example 5, the same amount of the above described compound (6) was used in place of Compound (3). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	7,200	100	500

It was noted that Compound (6) has an excellent sensitizing effect similar to Compound (3) of the Example 5.

EXAMPLE 7

In the same manner of Example 5, the same amount of the above described Compound (13) was used in place of Compound (3). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	6,300	100	500

Compound (13) also was effective as a sensitizer, similar to Compound (3) 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 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 normal temperature for 20 minutes, whereupon an aqueous phase and an isoamyl acetate phase were separated from each other. The aqueous phase was first removed, and 400 ml of water were added again to the remaining phase to wash the same by the decantation method. This operation was repeated three times, and then 400 ml of methanol were added to separate the 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 diameter of about 1 μ. 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.

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To 40 ml of the resulting silver salt-polymer dispersion were added the following components to produce a heat developable photographic composition, which was then applied to a polyethylene terephthalate film support in an amount of 1.2 g (coated silver content)/m² (support) to produce a heat developable photographic material (A).

Ammonium Iodide (8.5 wt% methanol solution)	1 ml	10
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	15
N-Ethyl-N'-dodecylurea (2.5 wt% methyl cellosolve solution)	2 ml	

A part 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 sensitizer of the present invention, the above Compound (5), and the latter (C) containing, as sensitizing dye, the same amount of the merocyanine dye (of the 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 percent tetrahydrofuran solution of a vinyl chloride-vinyl acetate copolymer (consisting of 95 wt percent of vinyl chloride and 5 wt percent of vinyl acetate), to form an over-coating film 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 amount of exposure 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 similar manner to Example 1. The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	4,300	100	200

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

EXAMPLE 9

In the same manner of Example 8, the amount of the above described Compound (11) was used in place of the Compound (5). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	3,800	100	200

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It is noted that Compound (11) has an excellent sensitizing effect similar to the Compound (5) of Example 8.

EXAMPLE 10

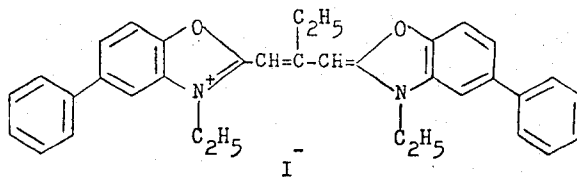
In the same manner of Example 8, the same amount of the above described Compound (12) was used in place of Compound (5). The results obtained are shown in the following Table.

	Material (A)	Material (B)	Material (C)
Relative Sensitivity	3,200	100	200

Compound (12) also was effective as a sensitizer, similar to Compound (5) of Example 8.

EXAMPLE 11

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



The results obtained are shown in the following Table. It is noted that the present sensitizer, Compound (1), displays a more excellent sensitizing effect due to the joint use with the cyanine dye.

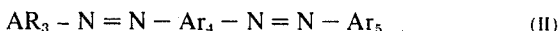
	Material (A)	Material (B)	Material (C)
Relative Sensitivity	19,000	100	600

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

- an organic silver salt,
- a catalytic amount of a photosensitive silver halide or a compound capable of reacting with said organic silver salt (a) to produce a photosensitive silver halide,
- a reducing agent,
- a binder, and
- as a sensitizer, at least one of the following Compounds (I) and (II):



wherein Ar_1 , Ar_2 , Ar_3 and Ar_5 each represents an aryl group and Ar_4 represents an arylene group, with the proviso that at least one of Ar_1 and Ar_2 , and at least one of Ar_3 , Ar_4 and Ar_5 is substituted with a $-SO_3M$ group, or a $-COOM$ group, M being a hydrogen atom, an alkali metal atom, an alkaline earth metal atom, or a $-NH_4$ group.

2. The heat developable photographic material as claimed in claim 1, wherein said Ar_1 , Ar_2 , Ar_3 and Ar_5 groups are substituted or unsubstituted phenyl groups, α -naphthyl groups or β -naphthyl groups, and said Ar_4 group is a substituted or unsubstituted phenylene group, biphenylene group or a naphthylene group.

3. The heat developable photographic material as claimed in claim 2, wherein said aryl and arylene groups are substituted with an alkyl group, a halogen atom, a hydroxyl group, an $-SO_3M$ group, a COOM group, an aryl group, a nitro group, an amino group, an alkylamino group, an arylamino group, an acry group, an alkoxy group, an arylsulfonyloxy group, or an alkylsulfonyloxy group.

4. The heat developable photographic material as claimed in claim 3, wherein said alkyl, alkoxy and acyl groups have 1 to 8 carbon atoms.

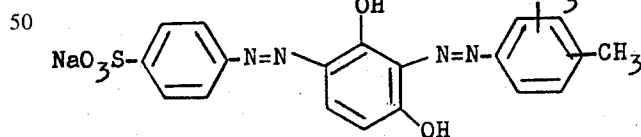
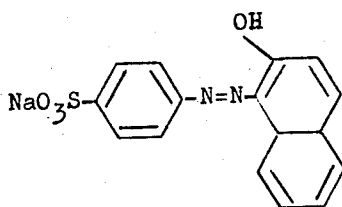
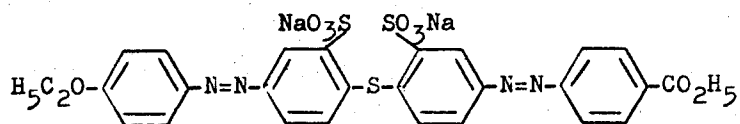
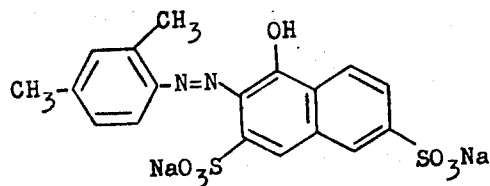
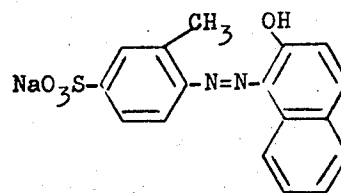
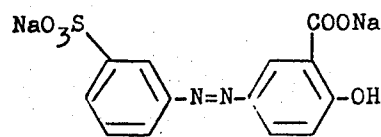
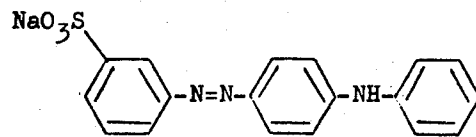
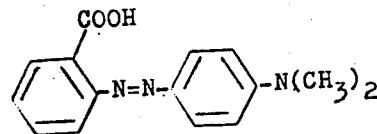
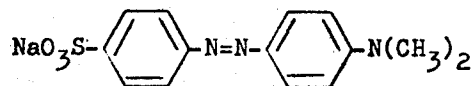
5. The heat developable photographic material as claimed in claim 4, wherein said alkyl, alkoxy and acyl groups have 1 to 4 carbon atoms.

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

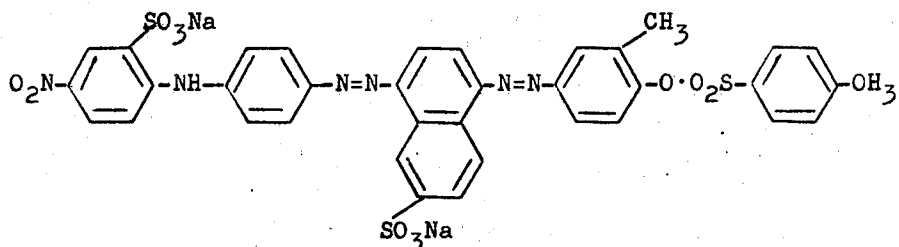
7. The heat developable photographic materials as claimed in claim 1, wherein said alkaline earth metal is Ca, Ba, or Mg.

8. The heat developable photographic material as claimed in claim 1, wherein said sensitizer (e) is selected from the group consisting of the following compounds

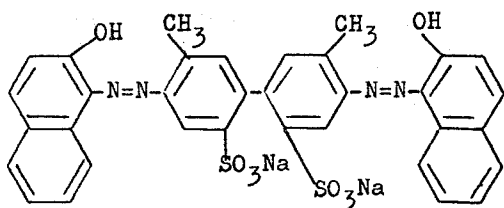
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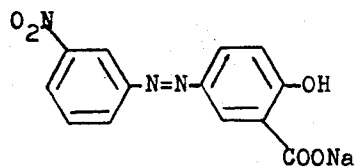


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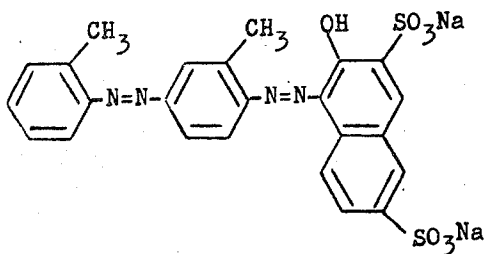


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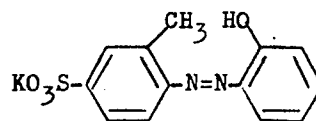
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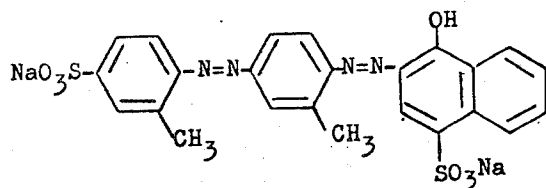


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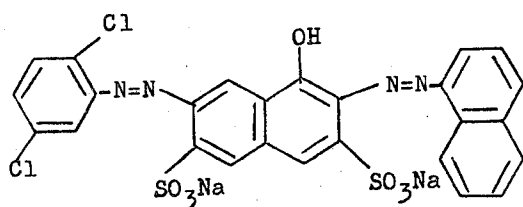
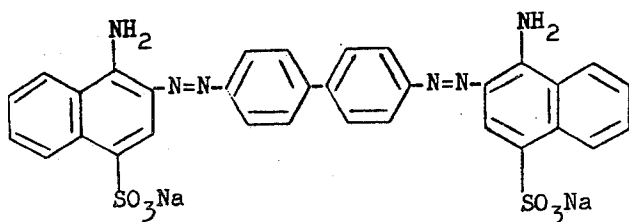
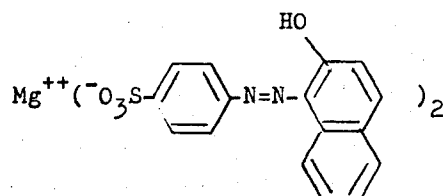


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and



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

50 10. The heat developable photographic material as claimed in claim 1, which further contains an optical sensitizing dye in an amount of about 10^{-6} to 10^{-2} per 1 mole of said organic silver salt.

55 11. The heat developable photographic material as claimed in claim 1, wherein said optical sensitizing dye is a cyanine dye or a merocyanine dye.

60 12. The heat developable photographic material as claimed in claim 1, including an over-coating layer on said photosensitive layer.

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