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[54] HEAT DEVELOPABLE LIGHT-SENSITIVE ELEMENTS

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[56] **References Cited**

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3,152,904	10/1964	Sorenson	96/95
3,429,706	2/1969	Shepard	96/95
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FOREIGN PATENTS OR APPLICATIONS

943,476	12/1963	Great Britain	96/114.1

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[57] **ABSTRACT**

A heat developable supported light-sensitive element wherein at least one layer thereon contains the silver salt of benzotriazole, a silver halide, or an inorganic halide capable of forming a silver halide by reaction with the silver salt of benzotriazole, a compound which decomposes upon heating to yield a basic material, and a reducing agent. In another embodiment, the layer further contains a compound capable of releasing water by heating.

Further described is a process for obtaining a print wherein the heat developable light-sensitive element(s) described above are heated for 1–30 seconds at 120°–170° C.

12 Claims, No Drawings

HEAT DEVELOPABLE LIGHT-SENSITIVE ELEMENTS

The present invention relates to a light-sensitive element and more particularly to a heat developable light-sensitive element containing a light-sensitive silver salt and one which is capable of forming images by heating.

In general, the most widely used photographic light-sensitive element uses silver halide. This is because photographic light-sensitive elements using a silver halide are generally excellent in the areas of sensitivity and gradation, as compared with electrophotographic light-sensitive elements and other light-sensitive elements. However, problems arise when using a silver halide photographic light-sensitive element. A developing solution must be employed for developing the photographic element after exposure and in order to prevent the developed photographic images from being discolored or faded and the background thereof from being blackened under usual light, the developed photographic element must be further subjected to several processing steps. The latter additional processings are usually called stopping, fixing or stabilizing. As will now be apparent, it is very desirable from the point of view of simplicity in processing to obtain photographic images by a completely dry process in silver halide photography and further to obtain stable and semipermanently preservable images without the necessity of fixing and other subsequent processings.

In order to meet this requirement, various efforts have hitherto been made. One process is the so-called monobath developing and fixing method in which the developing and fixing processes of conventional silver halide photographic processing are conducted in one process. See German Pat. No. 1,163,142; U.S. Pat. No. 2,875,048 and British Pat. No. 954,453.

As another improvement, a process has been provided wherein the processing of conventional silver halide photographic elements has been conducted by a dry system. This system has the advantage that since liquid chemicals for development and fixing need not be handled there are no dangers that hands or clothes may become contaminated with the chemicals as in the case of wet processing and, further, a photograph or copy can be directly obtained in the dried state. See German Pat. No. 1,174,159 and British Pat. Nos. 943,476 and 951,644.

However, the image obtained from conventional heat developable light-sensitive elements using a silver halide salt become blackened due to the printing out of the silver halide when the element, after development, is placed as is in a light place, which makes the discrimination of the image difficult. Therefore, it is necessary in such a system to process the developed photographic element with a stabilizing solution or a fixing solution to make the undeveloped silver halide particles light-insensitive or convert them into water-soluble materials, which are then removed by washing.

Still other techniques have been proposed in which a silver salt compound other than silver halide is employed. See U.S. Pat. No. 3,152,904 and Belgian Pat. No. 663,112.

The present invention relates generally to the last of the aforementioned proposals, i.e., a photographic light-sensitive element having a mixture of a light-insensitive and oxidizing organic silver salt, a slight amount of a light-sensitive silver salt, and more particularly to a photographic light-sensitive element containing a mixture of a silver salt of benzotriazale and a slight amount of a silver halide.

Accordingly, an object of the present invention is to provide a novel light-sensitive composition.

Another object of the present invention is to provide a novel process for reproducing images.

Still another object of the present invention is to provide a highly sensitive light-sensitive element capable of forming images by a dry process or by only heating without using any solutions in the developing process.

A further object of the present invention is to provide a light-sensitive element capable of providing light-stable images by developing, and one which is also capable of being

preserved substantially permanently after development without the necessary of conducting fixing and other procedures.

Other objects and advantages of the instant invention will become apparent from the ensuing specification.

The heat developable light-sensitive element of the present invention has a single-layer or multilayer containing a mixture of an organic silver salt which is light-insensitive and which can be reduced and a very slight amount of a light-sensitive silver salt, particularly a silver halide.

The light-sensitive element according to one embodiment of the present invention comprises a support bearing thereon at least one layer containing at least (a) a light-insensitive silver salt; (b) a material for providing light sensitivity, i.e., a silver halide, or an inorganic halide capable of producing a silver halide by reaction with the light-insensitive silver salt (a); (c) a compound capable of being decomposed into a basic material by heating and, if necessary, a compound capable of releasing water by heating; and (d) a reducing agent.

The light-sensitive element according to another embodiment of the present invention comprises a support bearing thereon at least one layer containing at least (a) a light-insensitive silver salt; (b) a material for providing light sensitivity, i.e., a small amount of a silver halide or an inorganic halide capable of forming a silver halide by reaction with the light-insensitive silver salt (a); (c) a metal oxide or hydroxide capable of being converted into a basic material by heating; and (d) a reducing agent together with, if necessary, at least one compound capable of releasing water by heating and a catalyst for accelerating the oxidation of the reducing agent.

Any of the above-mentioned light-sensitive elements of the present invention has color sensitivity and can provide stable images after exposure by a very simple dry process. Thus, if the images obtained by the heat development of the light-sensitive element after exposure are preserved as they are, the printout of silver halide scarcely proceeds, and moreover, if the thus developed light-sensitive element is processed with water or other suitable solvent, the progress of printout can be completely prevented and, hence, permanent images can be obtained.

The support used in this invention may be any physically and chemically stable flexible sheet such as metal foils, synthetic resin films (generally cellulose diacetate films, cellulose triacetate films, polyethylene terephthalate films, or polycarbonate films) and papers; but among the suitable papers, a paper having a good water-absorbing power is most suitable for use in the present invention.

As the light-insensitive silver salt, there may be illustrated: silver salts of organic compounds having imino groups, such as a silver salt of benzotriazole, a halogen substitute thereof or a nitro substitute thereof, carbazolyl silver, the silver salt of saccharin and the like. Among these salts, the silver salt of the halogen-substituted or nitro-substituted benzotriazole is light-insensitive but the heat development thereof is difficult; that is, such a silver salt is not effectively reduced by heating. Carbazolyl silver is also difficult to develop by heating. The silver salt of saccharin (o-sulfobenzoic acid imide) may be developed by heating but the contrast between the image and the background is low; that is, the formation of heat fog is increased. However, in the case of using the unsubstituted silver salt of benzotriazale, it can be developed by heating and the contrast between the image and background is high. Further, in the case of using the silver salt of benzotriazole, the element can be fixed by bathing with water, and if the temperature of the heat development is high, the density of the background is not increased even if the thus heat-developed light-sensitive element is allowed to stand in usual light for a long period of time. Accordingly, the silver salt of benzotriazole is the most suitable light-insensitive salt for the light-sensitive element of the present invention.

The silver salt of benzotriazole may be prepared by dissolving, for example, 59.5 g. of 1,2,3-benzotriazole into 2 liters of methanol and adding into the resulting solution an aqueous

solution of silver nitrate (85 g./200 ml.) with stirring at normal temperature. The thus-formed precipitate is washed with water by decantation 10 times, recovered by filtration, washed with water three times and then dried.

Further, by conducting the reaction of benzotriazole and silver nitrate in a solution containing at least one of the below-described binders to be used for the light-sensitive element, the size of the crystal of the silver salt can be controlled.

The inorganic halide capable of forming silver halide by reaction with the light-insensitive silver salt used in this invention is a water-soluble or organic solvent-soluble compound shown by the general formula MX_n wherein M represents hydrogen, ammonium or a metal, such as strontium, cadmium, zinc, tin, chromium, sodium, barium, iron, cesium, lanthanum, copper, calcium, nickel, magnesium, potassium, aluminum, antimony, gold, cobalt, mercury, lead, and beryllium; X represents a halogen atom, such as chlorine, bromine, and iodine; and n is the valency of M. Among them, the iodide is particularly preferable in the present invention since the silver salt formed by the reaction with the iodide has a property of being difficult to printout.

The light-insensitive organic silver salt containing a small amount of a silver halide or the above-mentioned organic halide may be, after being dispersed in the below-described binder solution, subjected to a sulfur sensitization, a reduction sensitization, or a noble metal sensitization as in the case of conducting the preparation of conventional photographic emulsions to increase the light sensitivity.

The compound to be used in this invention, which can be decomposed by heating into a basic material, can be an oxalate of an aliphatic amine such as dicyclohexylamine, an oxalate of an aromatic amine such as benzylamine, and an oxalate of a cyclic amine such as piperidine and morpholine. These salts of amines may be prepared by adding an aqueous or alcohol solution of an amine into an excessive amount of an aqueous or alcohol solution of oxalic acid and then filtering, washing and drying the thus-formed precipitate. These compounds may be used alone or as a mixture thereof.

When such an oxalate of the amine is heated, the oxalate is decomposed to release oxalic acid leaving a sufficient amount of the amine for providing the basicity necessary for the development.

The oxalates have excellent photographic properties as compared with the salts of other organic acids and the oxalates may be prepared easily. The decomposition temperature of these salts by heating is about 120° C. for the oxalate of dicyclohexylamine, about 125° C. for the oxalate of benzylamine, about 105° C. for the oxalate of piperidine, and about 135° C. for the oxalate of morpholine.

The metal oxide or hydroxide employed in the present invention to provide basicity by heating is the oxide or hydroxide of a metal belonging to groups 2 or 3 of the periodic table; for example, zinc oxide, aluminum oxide, magnesium oxide, zinc hydroxide, aluminum hydroxide, cadmium hydroxide, and magnesium hydroxide.

The above-mentioned metal oxide or hydroxide is also useful as an additive for improving the contrast between the image and the background.

The compound capable of releasing water by heating employed in this invention is a compound containing water of crystallization. Among such compounds, considering the temperature at which the water of crystallization is released and the fitness thereof to photographic emulsions, metal salts of acetic acid, such as lead acetate trihydrate, zinc acetate dihydrate, manganese acetate tetrahydrate, and magnesium acetate tetrahydrate are very effective. These compounds may be used alone or as a mixture thereof. The light-sensitive element of the present invention containing these compounds capable of releasing water by heating can provide a good photographic image as compared with those not containing such compounds.

The above-mentioned compound containing water of crystallization releases a part of the water of crystallization when heated to a temperature lower than 100° C. with the remaining water of crystallization being released at about 100° C. By measuring, by a differential thermal analysis, the temperature at which the above-mentioned compounds release the water of crystallization, it was confirmed that the temperatures are 50° C. and 100° C. for lead acetate trihydrate, 65° C. and 100° C. for cadmium acetate dihydrate, and 80° C. and 100° C. for zinc acetate dihydrate.

The reducing agent suitable employed in the present invention may be: an aromatic mono- or poly-hydroxyl compound or a derivative thereof, or an aromatic mono- poly-amino compound or a derivative thereof. For example, a developer used for usual photographic processing may be effectively used. Particularly effective examples of such reducing agents are hydroquinone, methylhydroquinone, chlorohydroquinone, bromohydroquinone, phenylhydroquinone, catechol, pyrogallol, hydroquinone monosulfonate, resorcinol, p-aminophenol, o-aminophenol, N-methyl-aminophenol one-half sulfate, 2-methoxy-4-aminophenol hydrochloride, 2,4-diaminophenol hydrochloride, sodium 1-amino-2-naphthol-6-sulfonate, p-oxyphenyl glycine, 2-hydroxyethyl-4-aminophenol, N,N-diethyl-p-phenylenediamine sulfite, 1-naphthylamine-7-sulfonic acid (-acid), M-acid, 1-hydroxy-4-methoxynaphthalene, 1-hydroxy-4-ethoxynaphthalene, 1,4-dihydroxynaphthalene, and 1-hydroxy-4aminonaphthalene. These compounds may be used alone or as a mixture thereof. Besides the above-mentioned compounds, 1-phenyl-3-pyrazolidone, hydroxylamine hydrochloride, and reducing saccharides (glucose, lactose, etc.) may be effectively used as the reducing agent. For effecting the heat development the oxidation reduction potential must be less than 500 m.v. (a standard hydrogen electrode).

The blending ratios of the above-mentioned (a) light-insensitive silver salt, (b) light-sensitivity-giving material; that is, the inorganic halide capable of forming a silver halide by reaction with the light-insensitive silver salt (a) or a small amount of a silver halide; and, in the case of the first embodiment of this invention, (c) the compound capable of being decomposed by heat into a basic material, and, if necessary, the compound capable of releasing water by heating; or in the second embodiment of this invention, (c') the metal oxide or hydroxide capable of being decomposed by heating into a basic material in conjunction with the compound capable of releasing water upon heating and (d) the reducing agent are generally influenced by the reducing power, the catalytic power, the molecular weight, and the like, but it is preferable that the proportion of the sensitivity-giving material (b) be from 1/100 to 1/10,000 part by weight based on the weight of light-insensitive silver salt (a); the proportion of compound (c) be from 10 to 1/100 part by weight based on the weight of the light-insensitive silver salt (a); the proportion of compound (c) be from 10 to 1/100 parts by weight based on the weight of the light-insensitive silver salt (a), the proportion of metal oxide or metal hydroxide (c') be from 20 to 1/100 parts by weight based on the weight of light-insensitive silver salt (a), and the proportion of reducing agent (d) be from 20 to 1/100 parts by weight based on the weight of light-insensitive silver salt (a).

If the proportion of the sensitivity-giving material is larger than the above-defined value, printing out of the silver halide tends to occur, while if less than the described value, the heat development becomes difficult. Further, if the proportion of (c) and (c') is larger than described, the preservability of the light-sensitive elements will be reduced, while, if less, the development becomes difficult. Also, if the proportion of reducing agent (d) is larger than the described value, printing out of silver halide tends to occur, while if less than the described value, the development becomes difficult. In the present invention, moreover, the composition containing the above-mentioned ingredients may contain, if necessary, a color sensitizer, a hardening agent, a developing accelerator, a matting agent, and a coating aid.

The composition containing the above-mentioned components is applied to a support, such as wood pulp paper, rag-containing paper, photographic paper, baryta paper, films, metal foils, dry glass plates, and the like. A part of or the entire composition may be coated on the support in separate layers. Further, in order to form a uniform and smooth coating of the composition on the support, it is preferable to use a suitable binder.

The binder which may be used in this invention is preferably translucent or transparent one so as not to lower the transmission of light therethrough. It is particularly preferable to employ photographic gelatin a solid high molecular weight material or resin. Suitable high molecular weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, polyvinyl pyrrolidone, ethyl cellulose, polyethylene glycol, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, a copolymer of butadiene and styrene, a copolymer of vinyl chloride and vinyl acetate, a copolymer of vinyl chloride, vinyl acetate and maleic acid, methacrylic resin, polyvinyl alcohol and derivatives thereof such as polyvinyl acetate.

The color sensitizer, coating aid, color-toning agent, matting agent, hardening agent, etc., may be any of those which are used for the preparation of conventional silver halide photographic sensitive elements.

In order to obtain images by using the thus-prepared light-sensitive elements of this invention, they are, after exposure using as a light source a tungsten lamp an ultraviolet lamp, heated in a suitable manner such as by passing the elements through two heated rollers, by placing the elements between two heated plates or by the irradiation of the elements with infrared rays.

In the first embodiment of the present invention, the compound capable of releasing water by heating releases water to wet the coating medium and simultaneously the compound capable of being decomposed by heating into a basic material is thermally decomposed to provide basicity to the coating medium. Consequently, the reducing agent, such as an aromatic mono- or poly-hydroxy compound, is activated and hence the exposed portion of the light-sensitive silver halide having a latent image acts as a reducing catalyst, whereby the light-insensitive silver salt is reduced to provide an image.

In the second embodiment of the present invention, the compound capable of becoming basic by heating provides the coating medium basicity and the oxidation reduction potential of the reducing agent is lowered to give photographic activity thereto. Accordingly, the exposed portion of the light-sensitive silver halide having a latent image acts as a reducing catalyst to reduce the light-insensitive silver salt, whereby an image is obtained.

Since the period of exposure is influenced by the kind and intensity of the light source and developing conditions, the kinds of reducing agent and other additives employed as well as the sensitivity of the light-sensitive silver salt, it may vary by a considerably wide range but the deviation is generally from 0.001 second to 5 minutes.

The development of the thus-exposed light-sensitive element is conducted by heating said element for 1 to 30 seconds at temperature above 80° C., preferably from 120° C. to 170° C.

By immersing the thus heat-developed light-sensitive element in a solvent for the reducing agent such as water, the excess reducing agent and the like are removed from the emulsion layer. Thus, no reduction occurs and hence even if the thus-treated light-sensitive element is exposed directly to sunlight, no density increase of the background is observed.

Although the washing effect may usually be weak, methanol or ethanol may be replaced with water for hastening the drying after the treatment.

If the developing temperature is comparatively higher, part or all of the reducing agent will be removed from the system by melting, evaporating or sublimating and hence even if the light-sensitive element subjected to the high-temperature development is allowed to stand as is or without the washing treatment, the density increase of the background is scarcely observed or is not observed at all.

Further, the density increase of the background when exposed in a bright place after development may be effectively prevented by incorporating in the emulsion layer of the heat-developable light-sensitive element an oxidizing catalyst capable of destroying the reducing agent by heating, such as titanium oxide, stannic chloride, antimony chloride, gallium azide, cadmium sulfide, cadmium selenide, etc., in an amount of 0.1 to 5 g. per 1 g. of the reducing agent.

As described above, since the light-sensitive elements of the present invention may be developed after exposure by the dry method and stable images can be obtained without the need of conducting fixing and other processing steps, it is now apparent that because of the present invention the reproduction process can be hastened and simplified.

Moreover, since the utilization of dry reproduction system eliminates the need of handling liquid chemicals for development and fixing, there is the advantage that copies or reproductions can be directly obtained in a dried state without being accompanied with the dangers of contaminating hands, clothes, etc., by handling liquid chemicals.

The following examples further illustrate the specific and preferred embodiments of the present invention.

EXAMPLE 1

Into a suitable amount of water were added 2 g. of the silver salt of benzotriazole, 7.5 g. of gelatin, 0.002 g. of strontium iodide, 1 g. of morpholine oxalate, 25 g. of lead acetate trihydrate, and 0.5 g. of hydroquinone and the resulting emulsion was, after the further addition of suitable amounts of a color sensitizer, an antifoggant, a coating aid, and a hardening agent, applied to a photographic paper. After exposure, the photographic element was developed by heating for 10 seconds at 140° C., immersed in tap water for 2 minutes, and dried. Thus, a stable image causing no printout phenomena when exposed to direct sunlight was obtained. Moreover, when the photographic element was developed, after exposure, by heating for 10 seconds at 160° C. a stable image causing no printout by direct exposure to sunlight was obtained without the need of water washing.

EXAMPLE 2

The following coating compositions were applied successively to a photographic paper per 25 square meters thereof;

a. an aqueous solution containing 5 g. of gelatin and 4 g. of morpholine oxalate,

b. an aqueous solution containing 5 g. of gelatin and 20 g. of catechol,

c. an aqueous dispersion containing 50 g. of the silver salt of benzotriazole and 180 g. of gelatin, and

d. an aqueous solution containing 10 g. of gelatin, 20 g. of lead acetate trihydrate, and 0.003 g. of cadmium chloride.

These coating liquids contained suitable amounts of a color sensitizer, a coating aid and a hardening agent.

After exposure, the resulting photographic element was developed by heating for 30 seconds at 160° C., immersed for 5 minutes in methanol and then dried. Thus, a stable image causing no printout by direct exposure to sunlight was obtained.

EXAMPLE 3

Into a suitable amount of water were added 2 g. of the silver salt of benzotriazole, 7.5 g. of gelatin, 0.0005 g. of silver iodide, 2.5 g. of piperidine oxalate, 25 g. of lead acetate trihydrate, and 0.5 g. of monomethyl hydroquinone and the resulting coating liquid was, after the further addition of suitable amounts of a color sensitizer, an antifoggant, a coating aid, and a hardening agent, applied to a photographic paper.

The thus-obtained photographic element was developed by heating at 160° C. for 10 seconds to provide a stable image causing no printout by the direct exposure to sunlight.

EXAMPLE 4

Into a suitable amount of water were added 2.5 g. of the silver salt of benzotriazole, 7.5 g. of gelatin, 0.002 g. of barium iodide, 1 g. of piperidine oxalate, and 25 g. of maltose and the resulting coating liquid was, after the further addition of a color sensitizer, an antifoggant and a coating aid, applied to a photographic paper. After exposure, the photographic element was developed by heating for 10 seconds at 160° C., immersed in water for 10 minutes, and then dried. Thus, a stable image causing no printout by the direct exposure thereof to sunlight was obtained.

EXAMPLE 5

Into a suitable amount of water were added 1 g. of the silver salt of benzotriazole, 4.5 g. of gelatin, 0.03 g. of strontium iodide, 0.5 g. of aluminum oxide, 15 g. of lead acetate trihydrate, and 0.2 g. of hydroquinone and the resulting coating liquid was, after the further addition of suitable amounts of a color sensitizer, an antifoggant, a coating aid and a hardening agent, applied to a photographic paper per 2 square meters thereof.

After exposure, the photographic light-sensitive element was developed for 5 seconds at 160° C. to provide a reproduction showing almost no density increase of background when exposed to direct sunlight. Moreover, when the sample was immersed for more than 1 second in water after development followed by drying, a stable image causing no density increase by the direct exposure to sunlight was obtained.

EXAMPLE 6

The following coating compositions were successively applied to a photographic paper per 25 square meters:

i. an aqueous dispersion containing 50 g. of gelatin and 5 g. of calcium hydroxide;

ii. an aqueous solution containing 5 g. of gelatin and 3 g. of pyrogallol;

iii. an aqueous dispersion containing 15 g. of the silver salt of benzotriazole and 45 g. of gelatin; and

iv. an aqueous solution containing 50 g. of gelatin, 200 g. of cadmium acetate dihydrate, and 0.3 g. of barium chloride.

These coating liquids contained suitable amounts of a color sensitizer, a coating aid and a hardening agent. After exposure, the thus-prepared photographic light-sensitive element was developed by heating for 30 seconds at 140° C., immersed for 5 minutes in methanol and then dried. The thus-processed sample showed no background density increase when exposed to direct sunlight.

EXAMPLE 7

Into a suitable amount of water were added 1 g. of the silver salt of benzotriazole silver, 4.5 g. of gelatin, 0.01 g. of silver iodide, 0.25 g. of aluminum oxide, 15 g. of zinc acetate, 0.2 g. of methyl hydroquinone, and 0.02 g. of titanium dioxide and the resulting coating composition was, after the addition of suitable amounts of a color sensitizer, an antifoggant, a coating aid and a hardening agent, applied to a photographic paper per 2 square meters thereof. After exposure, the thus-obtained light-sensitive element was developed for 5 seconds at 150° C. When the thus-developed sample was exposed to direct sunlight, no background density increase was observed.

EXAMPLE 8

The following coating liquids were applied in two layers to a polyethylene terephthalate film per 2 square meters thereof:

(Under layer) an aqueous dispersion containing 5 g. of gelatin and 1 g. of aluminum hydroxide and

(Upper layer) an aqueous dispersion containing 10 g. of gelatin, 0.02 g. of potassium iodide, 1 g. of the silver salt of benzotriazole and 0.3 g. of hydroquinone.

These coating liquids further contained suitable amounts of a color sensitizer, a coating aid and a hardening agent. After exposure, the thus-prepared light-sensitive element was developed by heating for 10 seconds at 170° C. immersed in water for 5 seconds and then dried to provide a stable image causing no background density increase when exposed to direct sunlight.

EXAMPLE 9

Into a suitable amount of an aqueous acetic acid solution were added 2 g. of the silver salt of benzotriazole, 9 g. of ethylcellulose, 0.02 g. of strontium iodide, 0.5 g. of zinc oxide, 0.3 g. of hydroquinone, and 0.01 g. of titanium dioxide and the resulting dispersion was, after the addition of suitable amounts of a color sensitizer and an antifoggant, applied to a polyethylene terephthalate film per 4 square meters.

After exposure, the thus-obtained light-sensitive element was developed by heating for 10 seconds at 150° C. to provide a reproduction causing almost no background density increase when exposed to direct sunlight.

EXAMPLE 10

Into a suitable amount of water were added 1 g. of the silver salt of benzotriazole, 9 g. of gelatin, 0.1 g. of strontium iodide, 0.6 g. of hydroquione, and 2 g. of aluminum hydroxide and the resulting coating composition was, after the addition of suitable amounts of a color sensitizer, an antifoggant, a coating aid, and a hardening agent, applied to a photographic paper per 4 square meters.

After exposure, the thus-obtained light-sensitive element was developed by heating for 10 seconds at 160° C. to provide a reproduction causing almost no background density increase when allowed to stand in situ in a bright place.

We claim:

1. A heat-developable light-sensitive element comprising a support bearing at least one layer thereon, said layer comprising:

a. the silver salt of benzotriazole;

b. at least one member selected from the group consisting of a silver halide and an inorganic halide represented by the formula MX_n, wherein M represents a member selected from the group consisting of a hydrogen atom, an ammonium group and a metal, X represents a halogen atom and n is the valency of M;

c. a compound capable of releasing a basic material upon heating comprising at least one member selected from a group consisting of an oxalate of an organic amine, a metal oxide and metal hydroxide, said metal being a member selected from the group consisting of metals of groups 2 and 3 of the periodic table;

d. a compound containing water of crystallization; and

e. a reducing compound comprising a member selected from the group consisting of aromatic mono- or polyhydroxyl compounds and derivatives thereof, and aromatic mono- or poly-amino compounds and derivatives thereof.

2. The heat-developable light-sensitive element as in claim 1 wherein said oxalate of an organic amine is dicyclohexylamine oxalate, benzylamine oxalate, piperidine oxalate, or morpholine oxalate.

3. The heat-developable light-sensitive element as in claim 1, wherein said compound containing water of crystallization is a member selected from the group consisting of lead acetate trihydrate, zinc acetate dihydrate and cadmium acetate dihydrate.

4. The heat-developable light-sensitive element as in claim 1 wherein said metal oxide is a member selected from the group consisting of zinc oxide, aluminum oxide and magnesium oxide, and said metal hydroxide is a member selected from the group consisting of zinc hydroxide, aluminum hydroxide, cadmium hydroxide and magnesium hydroxide.

5. The heat-developable light-sensitive element as in claim 1, wherein said reducing agent is a member selected from the group consisting of unsubstituted dihydroxybenzene, unsubstituted trihydroxybenzene, halogen-substituted dihydrox-

ybenzene, alkyl-substituted dihydroxybenzene, said alkyl having one to four carbon atoms, aryl-substituted dihydroxybenzene, and 1-phenyl-3-pyrazolidone.

6. The heat-developable light-sensitive element as in claim 1, wherein based on 1 part by weight of said silver salt of benzotriazole, the proportion of said inorganic halide varies from 10^{-2} to 10^{-4} part by weight, the proportion of said silver halide varies from 10^{-2} to 10^{-4} part by weight, the proportion of said metal oxide varies from 20 to 10^{-2} part by weight, the proportion of said metal hydroxide varies from 20 to 10^{-2} part by weight, the proportion of said oxalate of an organic amine varies from 10 to 10^{-2} part by weight, and the proportion of the reducing compound varies from 20 to 10^{-2} part by weight.

7. A heat-developable light-sensitive element comprising a support bearing at least one layer thereon, said layer comprising:

a. the silver salt of benzotriazole;

b. at least one member selected from the group consisting of a silver halide and an inorganic halide represented by the formula MX_n, wherein M represents a member selected from the group consisting of a hydrogen atom, an ammonium group and a metal, X represents a halogen atom and n is the valency of M;

c. a compound capable of releasing a basic material upon heating comprising at least one member selected from a group consisting of an oxalate of an organic amine, a metal oxide and metal hydroxide, said metal being a member selected from the group consisting of metals of groups 2 and 3 of the periodic table;

d. a compound containing water of crystallization;

e. a reducing compound comprising a member selected from the group consisting of aromatic mono- or polyhydroxyl compounds and derivatives thereof, and aromatic mono- or poly-amino compounds and derivatives thereof; and

f. a catalyst for accelerating the oxidation of said reducing compound.

8. The heat-developable light-sensitive element as in claim 7, wherein said catalyst for accelerating the oxidation of the reducing compound is a member selected from the group consisting of titanium oxide, stannic chloride, antimony chloride, gallium azide, cadmium sulfide, and cadmium selenide.

9. The heat-developable light-sensitive element as in claim 7, wherein said reducing compound is a member selected from the group consisting of unsubstituted dihydroxybenzene, unsubstituted trihydroxybenzene, halogen-substituted dihydroxybenzene, alkyl-substituted dihydroxybenzene, said alkyl having one to four carbon atoms, aryl-substituted dihydroxybenzene, and 1-phenyl-3-pyrazolidone.

10. The heat-developable light-sensitive element as in claim 7, wherein based on one part by weight of said silver salt of benzotriazole, the proportion of said inorganic halide varies from 10^{-2} to 10^{-4} part by weight, the proportion of said silver halide varies from 10^{-2} to 10^{-4} part by weight, the proportion of said metal oxide varies from 20 to 10^{-2} part by weight, the proportion of said oxalate of an organic amine varies from 10 to 10^{-2} part by weight and the proportion of said reducing compound varies from 20 to 10^{-2} part by weight.

11. A process for obtaining a print comprising exposing to light for from 0.001 second to 5 minutes a heat-developable light-sensitive element comprising a support bearing thereon at least one layer comprising:

a. the silver salt of benzotriazole;

b. at least one member selected from the group consisting of a silver halide and an inorganic halide represented by the formula MX_n, wherein M represents a member selected from the group consisting of a hydrogen atom, an ammonium group and a metal, X represents a halogen atom and n is the valency of M;

c. a compound capable of releasing a basic material upon heating comprising at least one member selected from a group consisting of an oxalate of an organic amine, a metal oxide and metal hydroxide, said metal being a member selected from the group consisting of metals of groups 2 and 3 of the periodic table;

d. a compound containing water of crystallization; and

e. a reducing compound comprising a member selected from the group consisting of aromatic mono- or polyhydroxyl compounds and derivatives thereof, and aromatic mono- or poly-amino compounds and derivatives thereof; and heating the exposed element for a period of time of from 1 to 30 seconds at a temperature of from 120° to 170° C.

12. A process for obtaining a print comprising exposing light for from 0.001 second to 5 minutes a heat-developable light-sensitive element comprising a support bearing thereon at least one layer comprising:

a. the silver salt of benzotriazole;

b. at least one member selected from the group consisting of a silver halide and an inorganic halide represented by the formula MX_n, wherein M represents a member selected from the group consisting of a hydrogen atom, an ammonium group and a metal, X represents a halogen atom and n is the valency of M;

c. a compound capable or releasing a basic material upon heating comprising at least one member selected from the group consisting of dicyclohexylamine oxalate, benzylamine oxalate, piperidine oxalate, morpholine oxalate, a metal oxide and a metal hydroxide, said metal being a member selected from the group consisting of metals of group 2 and 3 of the periodic table;

d. a compound containing water of crystallization comprising a member selected from the group consisting of lead acetate trihydrate, zinc acetate dihydrate and cadmium acetate dihydrate; and

e. a reducing compound comprising a member selected from the group consisting of aromatic mono- or polyhydroxyl compounds and derivatives thereof, and aromatic mono- or poly-amino compounds and derivatives thereof; and heating the exposed element for a period of time of from 1 to 30 seconds at a temperature of from 120° to 170° C.

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