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(54) Improved dry silver constructions.

(57) Disclosed are mercury-free, heat-developable photographic materials incorporating 1-hydroxy-benzotriazole hydrate and/or 1,2,3-benzotriazin-4(3H)one as anti-foggants. The image forming system of the photographic material also contains a light insensitive silver material; a light sensitive silver halide; a reducing agent for silver ion; and a binder. The dry silver construction exhibits excellent development latitude despite the fact that mercury has been excluded from the construction.

Field of the Invention

The present invention relates to dry silver photothermographic imaging materials and to certain anti-foggants used therein.

Background of the Invention

Silver halide photothermographic imaging materials, often referred to as "dry silver" compositions because no liquid development is necessary to produce the final image, have been known in the art for several years. See, for example, U.S. Pat. Nos. 3,457,075 and 3,839,049. These imaging materials typically contain a light insensitive material, a light sensitive material which generates silver when irradiated, and a reducing agent for silver ion. The light sensitive material is generally photographic silver halide which must be in catalytic proximity to the light insensitive silver source. In this context, "catalytic proximity" can be defined as an intimate physical association of these two materials, so that where silver nuclei or specks are generated by the irradiation or light exposure of the photographic silver halide, those nuclei are able to catalyze the reduction of the silver source by the reducing agent.

It has long been understood that silver is a catalyst for the reduction of silver ions and the silver-generating light sensitive halide catalyst progenitor may be placed into catalytic proximity with the silver source in a number of different fashions, such as partial metathesis of the silver source with a halogen-containing source (e.g., see U.S. Pat. No. 3,457,075); coprecipitation of the silver halide and silver source material (e.g., see U.S. Pat. No. 3,839,049), and any other method which intimately associates the silver halide and the silver source.

The light insensitive, reducible silver source used in this area of technology is a material which contains silver ions. The earliest and still preferred source comprises silver salts of long chain carboxylic acids, usually of from 10 to 30 carbon atoms. The silver salt of behenic acid or mixtures of acids of like molecular weight have been primarily used. Salts of other organic acids or other organic materials such as silver imidazolates have been proposed and U.S. Patent No. 4,260,677 discloses the use of complexes of inorganic or organic silver salts as image source materials.

In both photographic and photothermographic emulsions, exposure of the silver halide to light produces small clusters of silver atoms. The imagewise distribution of these clusters is known in the art as the latent image. This latent image generally is not visible by ordinary means and the light sensitive article must be further processed in order to produce a visual image. The visual image is produced by the catalytic reduction of silver ions which are in catalytic proximity to the specks of the latent image.

Research Disclosure No. 17029, "Photothermographic Silver Halide Systems," published June 1978, pp. 9-15, gives a brief history of photothermographic systems and discusses attempts to provide color to them. Many of these previously discussed patents and other art such as U.S. Pat. Nos. 3,180,731; 3,761,270; and 4,022,617 are noted as being relevant to the subject of providing dye density and color images to photothermographic emulsions.

One problem which has been encountered in the construction of these systems, though, is the traditional problem of fogging, i.e., an increase in background density of the produced image during development. In the past, fog development has been alleviated and controlled by the use of mercury in the dry silver constructions, e.g., see, for example, U.S. Pat. No. 4,585,734. There has been a need within the industry, however, for non-mercury containing photosensitive dry silver constructions which exhibit good development latitude and hence, minimize or avoid the fogging problem.

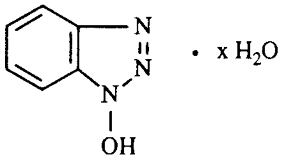
Summary of the Invention

In accordance with the present invention, it has been discovered the addition of 1-hydroxy-benzotriazole hydrate and/or 1,2,3-benzotriazin-4(3H)-one to non-mercury containing image-forming systems in photosensitive, heat-developable dry silver constructions affords very good development latitude and a substantial reduction in fogging. The development latitude of the dry silver construction is excellent despite the fact that mercury has been excluded from the construction.

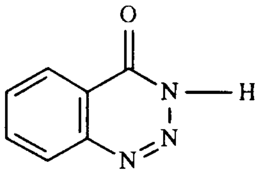
Other aspects, benefits, and advantages of the present invention are apparent from the detailed description, examples, and claims.

Detailed Description of the Invention

The use of a 1-hydroxy-benzotriazole hydrate and/or a 1,2,3-benzotriazin-4(3H)-one to the image forming systems of non-mercury containing dry silver constructions has been found to impart excellent development latitude to the dry silver construction and to substantially reduce fog formation. The structures of the two foregoing compounds are given below:



1-hydroxy-benzotriazole hydrate



1,2,3-benzotriazin-4(3H)-one

Both compounds are commercially available (e.g. from Aldrich Chemical Co. of Milwaukee, Wisconsin) and can be made by known methods of organic synthesis. See, for example, Beilstein, vol. 26, pages 41 and 163.

Preferably, one or both of the foregoing compounds are employed in an amount of from about 1-10 wt%, and most preferably in an amount of from about 5 wt% based upon the total weight of the image forming system.

Besides the above-disclosed anti-fogging agent(s), the heat-developable dry silver construction will also comprise a light insensitive silver source material; a light sensitive silver halide; a reducing agent for silver ion; and a binder.

The light insensitive silver source material ordinarily may be any material which contains a reducible source of silver ions. Silver salts of organic acids, particularly long chain (10 to 30, preferably 15 to 28 carbon atoms) fatty carboxylic acids are preferred in the practice of the present invention. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 and 10.0 are also useful in the present invention. The silver source material should constitute from about 20 to 70 percent by weight of the image forming system. Preferably, it is present as 30 to 55 percent by weight.

The silver halide may be any photosensitive silver halide such as silver bromide, silver iodide, silver chloride, silver bromoiodide, silver chlorobromoiodide, silver chlorobromide, etc., and may be added to the article in any fashion which places it in catalytic proximity to the silver source. The silver halide is generally present as 0.75 to 15 percent by weight of the image forming system, although larger amounts are useful. It is preferred to use from 1 to 10 percent by weight silver halide in the image forming system and most preferred to use from 1.5 to 7.0 percent.

The silver halide may be provided by in situ halidization or by the use of preformed silver halide. The use of sensitizing dyes for the silver halide is particularly desirable. These dyes can be used to match the spectral response of the emulsions to the spectral emissions of intensifier screens. It is particularly useful to use J-banding dyes to sensitive the emulsion as disclosed in U.S. Patent No. 4,476,220.

The reducing agent for silver ion may be any material, preferably organic material, which will reduce silver ion to metallic silver. Conventional photographic developers such as phenidone, hydroquinones, and catechol are useful, but hindered phenol reducing agents are preferred. The reducing agent should be present as 1 to 20 percent by weight of the image forming system. In a two-layer construction, if the reducing agent is in the second layer, slightly higher proportions of from about 2 to 20 percent tend to be more desirable.

The binder may be selected from any of the well-known natural and synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and terpolymers are, of course, included in these definitions. The polyvinyl acetals, such as polyvinyl butyral and polyvinyl formal, and vinyl copolymers, such as polyvinyl acetate/chloride are particularly desirable. The binders are generally used in a range of from 20 to 75 percent of the image forming system.

Toners such as phthalazinone, phthalazine and phthalic acid are not essential to the construction, but are highly desirable. These materials may be present, for example, in amounts of from 0.2 to 5 percent by weight of the image forming system.

The above-disclosed light sensitive composition can be coated on a support chosen from various kinds of materials in the form of a single layer or a multilayer to complete it as a heat-developable photographic material. Specific examples of such a support include various kinds of polymer materials, glass, wool cloth, cotton cloth, paper, metals (e.g. aluminum) and so on. Among these materials, materials capable of being worked upon a flexible sheet or roll are particularly preferable for the application to information recording materials from the handling point of view. Most suitable examples of the support in this invention include plastic films (e.g. a cellulose acetate film, a polyester film, a polyethylene terephthalate film, a polyamide film, a polyimide film, a triacetate film, and a polycarbonate film), and papers (e.g., plain paper, photographic raw paper, printing raw papers such as coated paper and art paper, baryta paper, resin-coated paper, pigment paper containing pigment like titanium dioxide, and paper sized with polyvinyl alcohol).

In the heat-developable photographic material, various kinds of auxiliary layers, e.g., a metal evaporated layer described in U.S. Pat. No. 3,748,137; a backing layer described in British Pat. No. 1,507,991 or Japanese Patent Application (OPI) Nos. 43130/76 or 129220/76; a backing layer containing a magnetic material described in Japanese Patent Application (OPI) No. 136099/75; an antistatic layer; and a subbing layer described in Japanese Patent Application (OPI) No. 87721/78 can be coated. Further, it is of great advantage to provide an overcoating polymer layer, as described in U.S. Pat. Nos. 3,933,508, 3,856,526, 3,856,527, and 3,893,860, because it can bring good results in that the transparency of each layer provided on the support is heightened, and moisture proofing characteristics or heat-resisting characteristics are improved. A suitable thickness of the overcoating polymer layer ranges from about 1 micron to about 20 microns. Suitable examples of the polymer for the overcoating layer include those described in each specification cited above as the polymers for the overcoating polymer layer. Among such polymers, polyvinyl chloride, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, polystyrene, methyl cellulose, ethyl cellulose, cellulose acetate butyrate, vinyl chloride-vinylidene chloride copolymer, carboxylic acid esters, cellulose diacetate, polyvinylidene chloride polycarbonate, gelatin, and polyvinyl alcohol are particularly preferable.

In the layer or the film containing the components of this invention, or each of the auxiliary layers, additives known in the art of heat-developable photographic materials, for example, a plasticizer, a matting agent, a surface active agent, a sensitizer, a brightening agent, a light absorbing agent, a filter dye, an antihalation dye, color couplers, a hardener, a lubricant, a development accelerating agent, and a stabilizer can be incorporated. Compound names and embodiments of these additives are described in *Product Licensing Index*, Vol. 92, No. 9232, p. 107 (Dec. 1971), Japanese Patent Application (OPI) Nos. 33615/78, 119623/75, 57619/75 and 27923/76, and U.S. Pat. Nos. 3,769,019, 3,821,001, 3,667,959, 3,871,887, 3,885,965, 4,021,250, 4,036,650, 3,531,286, and 3,764,328.

Processes for preparing the heat-developable photographic materials of this invention are illustrated below. An organic silver salt prepared using one of the known methods is optionally washed with water, an alcohol or the like and then mixed with a light sensitive silver halide to make a mixture in which both are present in a close contact state. In another process, a silver halide and an organic silver salt may be produced at the same time. In the most preferable way, a part of an organic silver salt is converted into silver halide using a silver halide forming component. When using sensitizing dyes, it is preferable to add the sensitizing dyes in the form of a solution after the above-described mixing step to the resulting mixture. The mixture of the organic silver salt and silver halide is desirably prepared in the form of a polymer dispersion in a solution of a polymer which can function as the binder afterward. This polymer can be added in any of the steps, such as the step of preparing the organic silver salt, the step of mixing with the silver halide or the step of preparing the silver halide. The polymer dispersion of the organic silver salt and the silver halide is molded in a film or coated in a layer on a support, and other components of this invention may be incorporated into that film or a layer provided on that layer. More preferably, other components to be employed in this invention, i.e., at least a reducing agent and binder are added to the above-described polymer dispersion of the organic silver salt and the silver halide to prepare a heat-developable photographic composition, and the resulting composition is poured and spread into a film or coated in a layer on a support using a known method. When coating the composition, various kinds of coating methods, for example, a dip coating method, an air knife coating, a curtain coating method, and a hopper coating method can be employed. In addition, various kinds of auxiliary layers, for example, a subbing layer, an overcoating layer, etc., can be optionally coated on prior to, simultaneously with or subsequently to the coating of the heat-developable photographic composition using a similar method to one of the above-described methods.

Solvents to be used for the coating solutions may be arbitrarily selected. For instance, noncombustible solvents as described in British Pat. No. 1,422,145 can be used.

Optionally, printing can be carried out on the surface or the back of the support, or on a layer provided on the support. Therefore, the materials of this invention on which prescribed patterns are printed can be applied to a (season) ticket, a postcard and other correspondence.

The thus prepared heat-developable photographic material is cut in a size suitable for use and subjected to imagewise exposure. Preheating (up to 80°C-140°C) may be carried out prior or during to the exposing step, if necessary. Suitable light sources for imagewise exposure include a tungsten lamp, a fluorescent lamp for a copier as used mainly for exposure of diazo type light-sensitive materials, a mercury lamp, an iodine lamp, a xenon lamp, a cathode ray tube (CRT) light source, a laser light source, etc. As for an original, not only line images like drafting, but also photographic images having gradation can be employed. Printing may be carried out using a contact printing method as an original is superposed directly on the photographic material, or using a reflection printing method or an enlarging printing method. A suitable exposure is determined depending upon the sensitivity of the photographic material used. It is about 1 lux. sec. in the case of high-speed photographic materials, and about 10^3 lux. sec. in the case of low-speed ones. The thus imagewise exposed photographic material can be developed only by heating (at a temperature higher than about 80 ° C, and most preferably ranging from about 100 ° C to about 150 ° C). The printing time is adjusted to a value within the range of 1 sec. to 60 sec. It is preferably determined depending upon the heating temperature adopted. Usually, about 5 sec. to about 40 sec. are suitable for 120 ° C; about 2 sec. to about 20 sec. for 130 ° C; and about 1 sec. to about 10 sec. for 140 ° C. Heating may be carried out using various means. For example, the photographic material may be simply made to come into contact with a hot plate or drum, or may be made to pass through a heated space as circumstances require. Further, a high frequency wave-induced heating means, or a laser beam-induced heating means may be adopted.

The following non-limiting examples further illustrate the present invention.

Example 1

A dispersion of silver behenate half soap was prepared at 15% solids in ethanol by homogenization. This dispersion was then prepared for coating by the addition of more solvent, halide, resin and sensitizing dye. The following silver soap dispersion was used: 165 grams of the 15% silver soap dispersion was mixed with 0.1 grams of Butvar™ B-72 (Monsanto) polyvinyl butyral. 325 grams of ethyl alcohol was added and mixed until homogeneous. 6 ml. of 0.1 mole zinc bromide dissolved in 20 ml of methyl alcohol was added. An additional 26 g of Butvar™ B-72 was added with mixing and 1.0 g of 3M fluorochemical FC431 (3M) was added as a coating aid. To 20 g of the above dispersion was added the following: 0.3 grams of 2-(4-hydroxy-3,5-dimethoxy)-4,5-bis(para-methoxyphenyl)imidazole, 0.2 grams of phthalazinone and 0.1 g of 1,2,3-benzotriazin-4(3H)-one and a blue merocyanine sensitizing dye. The formulation was then coated at 5 mils wet thickness and dried 5 min. at 180 ° F. Samples were exposed on an EG&G sensitometer through a 0-4 continuous wedge and developed on a heated platten at 280 ° F for 10 seconds. A Dmin of 0.16 and a Dmax of 1.06 were obtained with a blue status A filter on a MacBeth™ densitometer. A similar formula not containing 1,2,3-benzotriazin-4(3H)-one fogged after 3 seconds development at 280 ° F and gave no image.

Example 2

Example 1 was repeated except that to 20 g of the dispersion, 0.15 grams of a magenta developer dye, 0.2 g of phthalazinone, and 0.3g of 1,2,3-benzotriazin-4(3H)-one along with a green merocyanine sensitizing dye were added. A magenta image having a Dmin of 0.11 and a Dmax of 1.58 to the green filter of the MacBeth densitometer was produced.

Example 3

Example 1 was repeated except that to the 20 g of silver dispersion, was added 0.3 g of 3'5'-ditertbutyl-4'-hydroxybenzoyl-3,7-di(n,n-diethylamino)-oxazine (a cyan dye developer), 0.2 g of 4-methyl-phthalic acid, and 0.05 grams of 1,2,3-benzotriazin-4(3H)-one along with a red merocyanine sensitizing dye. This produced a cyan imaging giving a Dmin of 0.18 and a Dmax of 2.04 to the red filter of the MacBeth densitometer when processed as in Example 1.

Example 4

Example 1 was repeated except that to 20 grams of the silver dispersion a black and white developer, 0.3 grams Nonox W50, 0.2 grams phthalazinone, and 0.07 grams of 1,2,3-benzotriazin-4(3H)-one were added. When coated and processed the same as in Example 1, a black image with a Dmin of 0.13 and a Dmax of 1.5 to the neutral density filter of a MacBeth™ densitometer was produced.

Example 5

Example 1 was repeated except that to 20 grams of the silver dispersion was added 0.15 gram of 3',5'-dimethoxy-4'-hydroxy-propiophenone yellow developer, 0.5 gram of phthalazinone and 0.05 gram of 1-hydroxy-benzotriazole hydrate (Aldrich Chemical). After coating and processing as in Example 1, a blue filter on the MacBeth™ densitometer produced a Dmin of 0.28 and a Dmax of 1.24. A sample made the same way as Example 5, except that no 1-hydroxy-benzotriazole hydrate was used, fogged upon processing giving no image.

Reasonable modifications and variations are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined by the claims.

Claims

1. A mercury-free, heat-developable photographic material containing an image forming system comprising:
   (a) a light insensitive silver source material;
   (b) a light sensitive silver halide;
   (c) a reducing agent for silver ion;
   (d) at least one anti-foggant selected from the group consisting of a 1-hydroxy-benzotriazole hydrate and a 1,2,3-benzotriazin-4-(3H)-one; and
   (e) a binder.

2. A photographic material according to Claim 1 wherein said light insensitive silver source material, light sensitive silver halide, reducing agent for silver ion, anti-foggant, and binder are coated on a support.

3. A photographic material according to Claim 1 wherein said light insensitive silver source material is the silver salt of a C_{10}-C_{30} carboxylic acid and the material is free of mercury.

4. A photographic material according to Claim 1 wherein said light insensitive silver source material is present in said image forming system in an amount of from about 20-70 weight percent.

5. A photographic material according to Claim 1 wherein said light sensitive silver halide is present in said image forming system in an amount of from about 0.75 to 15 weight percent.

6. A photographic material according to Claim 1 wherein said light sensitive silver halide comprises silver bromide and the material is free of mercury.

7. A photographic material according to Claim 1 wherein said reducing agent for silver ion is present in said image forming system in an amount of from about 1 to 20 weight percent.

8. A photographic material according to Claim 1 wherein said anti-foggant is 1-hydroxy-benzotriazole hydrate.

9. A photographic material according to Claim 1 wherein said anti-foggant is 1,2,3-benzotriazin-4(3H)-one.

10. A photographic material according to Claim 1 wherein said image forming system further comprises a toner.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1801

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 194 025 (MINNESOTA MINING AND MANUFACTURING COMPANY) * claims 1,5 * ---	1-7,9,10	G03C1/498
X	PATENT ABSTRACTS OF JAPAN vol. 4, no. 31 (P-2)(513) 18 March 1980 & JP-A-55 004 060 (ASAHI KASEI KOGYO K.K.) 12 January 1980 * abstract * ---	1-7,9,10	
Y	US-A-4 728 600 (H.HARA, T.AONO) * compound (1) * ---	1-8,10	
Y	EP-A-0 204 197 (FUJI PHOTO FILM COMPANY LTD.) * compound I-8 on p.8; claims * ---	1-8,10	
Y	STURGE,WALWORTH,SHEPP (EDS.) 'Imaging Processes and Materials, Rev. 8th Ed. of Neblette's Handbook of Photography and Reprography' 1989 , VAN NOSTRAND REINHOLD , NEW YORK, US * chapter 9: 'Thermally Processed Silver Systems': p.288, righthand column 1.22-25 * -----	1-8,10	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)** G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 MAY 1992	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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