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3,579,345

DIRECT POSITIVE EMULSIONS SENSITIZED WITH PYRYLIUM AND/OR THIAPYRYLIUM SALTS

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19 Claims

ABSTRACT OF THE DISCLOSURE

Pyrylium, thiapyrylium or selenapyrylium salts are incorporated in direct positive photographic silver halide emulsions.

This application is a continuation-in-part of copending application Ser. No. 609,762 filed Jan. 17, 1967, now abandoned.

This invention relates to novel photographic materials, and more particularly to new and improved direct positive photographic silver halide emulsions containing certain pyrylium, thiapyrylium or selenapyrylium salt dyes as electron acceptors and spectral sensitizers therefor, and to photographic elements prepared with such emulsions.

It is known that direct positive images can be obtained with certain types of photographic silver halide emulsions. As shown in British Pat. 723,019, published Feb. 2, 1955, one photographic emulsion of this type comprises an electron acceptor and silver halide grains which are fogged with a combination of a reducing agent and a compound of a metal more electropositive than silver such as, for example, a compound of gold, palladium or platinum. However, known materials of this type have required blue light exposure and have not exhibited the speed required for many applications of photography. It is evident, therefore, that a means for increasing the photographic speed and for extending the spectral sensitivity to the green and red wavelength radiations of direct positive photographic materials would be highly desirable in the art.

It is, accordingly, an object of this invention to provide new and improved direct positive photographic silver halide emulsions.

Another object of this invention is to provide novel light-sensitive photographic elements comprising a support material having thereon at least one layer of a novel direct positive photographic emulsion.

Other objects will become apparent from this disclosure and the appended claims.

I have now made the discovery that new and improved direct positive photographic silver halide emulsions, and more particularly the fogged type emulsions, are produced by incorporating into such emulsions a pyrylium, thiapyrylium or selenapyrylium salt dye. These dyes function as electron acceptors and spectral sensitizers, and thereby provide direct positive emulsions that show excellent speed together with spectral sensitization extended in many instances up to 720 mμ. The direct positive images produced therewith are clear and sharp with excellent contrast.

In accordance with the invention, novel and improved direct positive photographic silver halide emulsions are prepared by incorporating one or more of the dyes of the invention into a suitable fogged silver halide emulsion. The emulsion can be fogged in any suitable manner, such as by light or with chemical fogging agents, e.g., stannous chloride, formaldehyde, thiourea dioxide and the like. The emulsion may be fogged by the addition thereto of a reducing agent such as thiourea dioxide and

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a compound of a metal more electropositive than silver such as a gold salt, for example, potassium chloroaurate, as described in the aforementioned British Pat. 723,019 (1955).

Typical reducing agents that are useful in providing such emulsions include stannous salts, e.g., stannous chloride, hydrazine, sulfur compounds such as thiourea dioxide, phosphonium salts such as tetra(hydroxymethyl) phosphonium chloride, and the like. Typical useful metal compounds that are more electropositive than silver include gold, rhodium, platinum, palladium, iridium, etc., preferably in the form of soluble salts thereof, e.g., potassium chloroaurate, auric chloride (NH₄)₂PdCl₆ and the like.

Useful concentrations of reducing agent and metal compound (e.g., metal salt) can be varied over a considerable range. As a general guideline, good results are obtained using about .05 to 40 mg. reducing agent per mole of silver halide, and 0.5 to 15.0 mg. metal compound per mole of silver halide. Best results are obtained at lower concentration levels of both reducing agent and metal compound.

The concentration of added dye can vary widely, e.g., from about 50 to 2,000 mg. and preferably from about 400 to 800 mg. per mole of silver halide in the direct positive emulsions.

As used herein, and in the appended claims, "fogged" refers to emulsions containing silver halide grains which produce a density of at least 0.5 when developed, without exposure, for 5 minutes at 68° F. in developer Kodak DK-50 having the composition set forth below, when the emulsion is coated at a silver coverage of 50 mg. to 500 mg. per square foot.

DEVELOPER

	G.
N-methyl-p-aminophenol sulfate	2.5
Sodium sulfite (anhydrous)	30.0
Hydroquinone	2.5
Sodium metaborate	10.0
Potassium bromide	0.5
Water to make 1.0 l.	

The dyes of this invention are also advantageously incorporated in direct positive emulsions of the type in which a silver halide grain has a water-insoluble silver salt center and an outer shell composed of a fogged water-insoluble silver salt that develops to silver without exposure. The dyes of the invention are incorporated, preferably, on the outer shell of such emulsions. These emulsions can be prepared in various ways, such as those described in Berriman U.S. patent application Ser. No. 448,467, filed Apr. 15, 1965 now U.S. Pat. 3,367,778, issued Feb. 6, 1968. For example, the shell of the grains in such emulsions may be prepared by precipitating over the core grains a light-sensitive water-insoluble silver salt that can be fogged and which fog is removable by bleaching. The shell is of sufficient thickness to prevent access of the developer used in processing the emulsions of the invention to the core. The silver salt shell is surface fogged to make it developable to metallic silver with conventional surface image developing compositions. The silver salt of the shell is sufficiently fogged to produce a density of at least about 0.5 when developed for 6 minutes at 68° F. in Developer A below when the emulsion is coated at a silver coverage of 100 mg. per square foot. Such fogging can be effected by chemically sensitizing to fog with the sensitizing agents described for chemically sensitizing the core emulsion, high intensity light and the like fogging means well known to those skilled in the art. While the core need not be sensitized to fog, the shell is fogged. Fogging by means of a reduction sensitizer, a noble metal salt such as gold salt plus a reduction sensitizer, a sulfur

sensitizer, high pH and low pAg silver halide precipitating conditions, and the like can be suitably utilized. The shell portion of the subject grains can also be coated prior to fogging.

DEVELOPER A

	G.
N-methyl-p-aminophenol sulfate -----	2.5
Ascorbic acid -----	10.0
Potassium metaborate -----	35.0
Potassium bromide -----	1.0
Water to 1 liter.	
pH of 9.6.	

Before the shell of water-insoluble silver salt is added to the silver salt core, the core emulsion is first chemically or physically treated by methods previously described in the prior art to produce centers which promote the deposition of photolytic silver, i.e., latent image nucleating centers. Such centers can be obtained by various techniques as described herein. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Sauvenir in *Science et Industries Photographiques*, vol. XXVIII, January 1957, pages 1 to 23 and January 1957, pages 57 to 65 are particularly useful. Such chemical sensitization includes three major classes, namely, gold or noble metal sensitization, sulfur sensitization, such as by a labile sulfur compound, and reduction sensitization, e.g., treatment of the silver halide with a strong reducing agent which introduces small specks of metallic silver into the silver salt crystal or grain.

The dyes of this invention are highly useful electron acceptors in high speed direct positive emulsions comprising fogged silver halide grains and a compound which accepts electrons, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,794, filed concurrently herewith and titled "Photographic Reversal Materials III," now abandoned, and continuation-in-part application Ser. No. 619,909, filed Mar. 2, 1967, now U.S. Pat. 3,501,306, issued Mar. 17, 1970. The fogged silver halide grains of such emulsions are such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about one upon processing for six minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for six minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

Potassium cyanide—50 mg.
Acetic acid (glacial)—3.47 cc.
Sodium acetate—11.49 g.
Potassium bromide—119 mg.
Water to 1 liter

The grains of such emulsions will lose at least about 25% and generally at least about 40% of their fog when bleached for ten minutes at 68° F. in a potassium cyanide bleach composition as described herein. This fog loss can be illustrated by coating the silver halide grains as a photographic silver halide emulsion on a support to give a maximum density of at least 1.0 upon processing for six minutes at about 68° F. in Kodak DK-50 developer and comparing the density of such a coating with an identical coating which is processed for six minutes at 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at 68° F. in the potassium cyanide bleach composition. As already indicated, the maximum density of the unbleached coating will be at least 30% greater, generally at least 60% greater, than the maximum density of the bleached coating.

The silver halides employed in the preparation of the photographic emulsions useful herein include any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromiodide, silver chlorobromide, and the like.

Silver halide grains having an average grain size less than about one micron, preferably less than about 0.5 micron, give particularly good results. The silver halide grains can be regular and can be any suitable shape such as cubic or octahedral, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,778, filed concurrently herewith and titled "Direct Positive Photographic Emulsions I," now abandoned, and continuation-in-part application Ser. No. 619,909, filed Mar. 2, 1967, now U.S. Pat. 3,501,306, issued Mar. 17, 1970. Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in Illingsworth U.S. patent application Ser. No. 609,790, filed concurrently herewith and titled "Photographic Reversal Emulsions II," now abandoned, and continuation-in-part application Ser. No. 619,948, filed Mar. 2, 1967, now U.S. Pat. 3,501,305, issued Mar. 17, 1970. For example, at least 95%, by weight, of the photographic silver halide grains can have a diameter which is within about 40%, preferably within about 30% of the mean grain diameter, i.e., average grain size, can be determined using conventional methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series" in *The Photographic Journal*, vol. LXXIX, 1949, pages 330-338. The fogged silver halide grains in these direct-positive photographic emulsions of this invention produce a density of at least 0.5 when developed without exposure for five minutes at 68° F. in Kodak DK-50 developer when such an emulsion is coated at a coverage of 50 to about 500 mg. of silver per square foot of support. The preferred photographic silver halide emulsions comprise at least 50 mole percent bromide, the most preferred emulsions being silver bromiodide emulsions, particularly those containing less than about ten mole percent iodide. The photographic silver halides can be coated at silver coverages in the range of about 50 to about 500 milligrams of silver per square foot of support.

In the preparation of the above photographic emulsions, the dyes, reducing agents and metal compounds of the invention are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes and other addenda in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add them from solutions in appropriate solvent or by immersion of the coated element in the solution, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, water, etc., alone or in admixtures, have proven satisfactory as solvents for this purpose. The type of silver halide emulsions that can be sensitized with the new dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc. and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ether, partially hydrolyzed cellulose acetate, and the like.

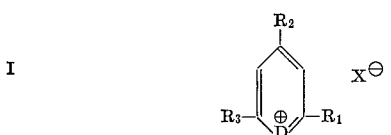
The dyes, reducing agents and metal compounds of the invention can be used with emulsions prepared, as indicated above, with any of the light-sensitive silver halide salts including silver chloride, silver bromide, silver chlorobromide, silver bromiodide, silver chlorobromiodide, etc. Particularly useful are direct positive fogged emulsions in which the silver salt is a silver bromohalide comprising more than 50 mole percent bromide. The dyes of this invention are also useful in emulsions which contain color formers.

The novel emulsions of this invention may be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as polyethylene terephthalate, paper, baryta

coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene coated paper, which may be electron bombarded to promote emulsion adhesion, to produce the novel photographic elements of the invention.

Pyrylium, thiapyrylium and selenapyrylium salt dyes, including benzo- and naphtho-pyrylium, thiapyrylium and selenapyrylium salt dyes function as useful electron acceptors and spectral sensitizers for preparing the direct positive photographic emulsions of the invention. Particularly useful dyes are those that are trisubstituted on the carbon atoms in the 2-, 4-, and 6-positions of the nucleus thereof, such as with the organic radicals as described in Formula I.

One highly useful class of dyes which function especially well as electron acceptors and spectral sensitizers for fogged direct positive photographic emulsions of the invention include certain pyrylium, thiapyrylium and selenapyrylium compounds represented by the following general formula:

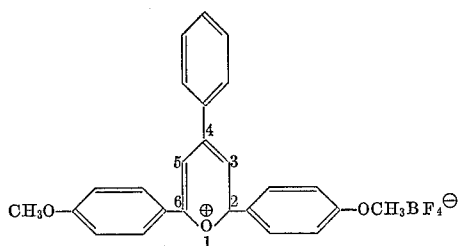


wherein D represents an oxygen, sulfur or selenium atom, X represents an acid anion which has no adverse effects on the emulsion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate, fluoroborate, sulfoacetate, borofluoride, trifluoroacetate, etc., and R₁, R₂ and R₃ each represents an alkyl group including substituted alkyl (preferably a lower alkyl containing from 1-4 carbon atoms), e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, benzyl, phenethyl, a styryl group such as styryl, o-, p- and m-methoxystyryl, o-, p- and m-styrylstyryl, N-phenylacridanylideneethyl group, etc., etc.; an alkoxy group, preferably a lower alkoxy, e.g., methoxy, ethoxy, propoxy, isopropoxy, butoxy, etc.; an aryl group (including substituted aryl), e.g., phenyl, o-, p- and m-tolyl, o-, p- and m-ethylphenyl, etc., an alkoxyphenyl group, e.g., o-, p- and m-anisyl, o-, p- and m-ethoxyphenyl, etc., a hydroxyalkoxyphenyl group such as β-hydroxyethoxyphenyl, ω-hydroxyamyloxyphenyl, ω-hydroxybutoxyphenyl, etc., a carboxyalkoxyphenyl group such as carboxymethoxyphenyl, β-carboxyethoxyphenyl, ω-carboxybutoxyphenyl, etc., a biphenyl group, an azidophenyl such as o-, p- and m-azidophenyl, etc., an acylamidophenyl group such as o-, p- and m-acetamidophenyl, p-propionamidophenyl, etc., an alkoxy-carbonylphenyl group such as methoxycarbonylphenyl, ω-butoxycarbonylphenyl, chloromethoxycarbonylphenyl, bromomethoxycarbonylphenyl, etc., a naphthyl group such as 1- or 2-naphthyl, etc., an arylalkenyl group typically having 1-20 carbon atoms such as 4-phenylbutadienyl, 3-methyl-4-phenylbutadienyl, etc., and the like.

The pyrylium, thiapyrylium and selenapyrylium dye compounds defined by formula I above are illustrated more specifically by the following Examples 1, 2 and 3 and by those listed in Table 1 hereinafter.

EXAMPLE 1

2,6-di-p-methoxyphenyl-4-phenylpyrylium fluoroborate



This compound was evaluated by the procedure set forth immediately below and found to extend the spectral sensitivity to 580 mμ with a peak at 540 mμ, and to give high quality reversal images.

Excellent magenta images are obtained when the color former 1-(2,4,6-trichlorophenyl)-3,3'-(2'',4''-di-t-amylphenoxy-acetamido-benzimidazo-5-pyrazolone is incorporated in the emulsion of this example, the emulsion is coated on a support, exposed to a tungsten source through Wratten filter No. 61 and No. 16, and reversal processed as described in Graham et al. U.S. Pat. 3,046,129, issued July 24, 1962, in Example(a) col 27, lines 27 et seq. except that black-and-white (MQ) development is omitted, the color development is reduced to one minute and is conducted in total darkness until after fixing.

Evaluation procedure

A gelatin silver bromide emulsion (2.5 mole percent of the halide being iodide) and having an average grain size of about 0.2 micron is prepared by adding an aqueous solution of potassium bromide and potassium iodide, and an aqueous solution of silver nitrate, simultaneously to a rapidly agitated aqueous gelatin solution at a temperature of 70° C., over a period of about 35 minutes. The emulsion is chill-set, shredded and washed by leaching with cold water in the conventional manner. The emulsion is reduction-gold fogged by first adding 0.2 mg. of thiourea dioxide per mole of silver and heating for 60 minutes at 65° C. and then adding 4.0 mg. of potassium chloroaurate per mole of silver and heating for 60 minutes at 65° C. The resulting emulsion is coated on acetate film support at a coverage of 100 mg. of silver and 400 mg. of gelatin per square foot of support.

A sample of the coated support is then exposed on a Bausch and Lomb Spectrograph for 5 seconds at a slit-width of 1 mm., and processed for 6 minutes at room temperature in Kodak D-72 developer which has the following composition:

	G.
N-methyl-p-aminophenol sulfate	3.0
Sodium sulfite (anhydrous)	45.0
Hydroquinone	12.0
Sodium carbonate (monohydrate)	80.0
Potassium bromide	2.0
Water to make 1.0 liter.	

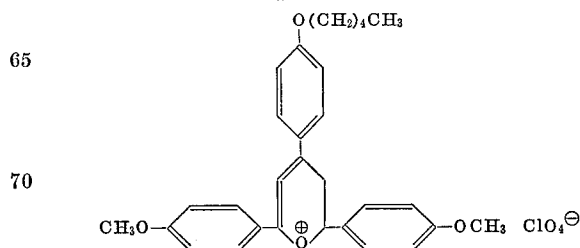
then fixed, washed and dried.

For evaluation of the dyes, the specific compound is dissolved in a solution containing equal amounts by weight of water, acetone and dimethylformamide so that approximately a 0.1% (by wt.) solution of the photo-oxidant is obtained.

Another sample of the above emulsion coated support is immersed in the said solution for 30 seconds, then dried and exposed on a Bausch and Lomb Spectrograph for 5 seconds at a slit-width of 5 mm., and finally developed in Kodak D-72 developer for 1.5 minutes, followed by fixation in a conventional fixing bath. The speed was determined from the densitometric measurements.

EXAMPLE 2

2,6-bis-(p-anisyl)-4-(p-n-amlyoxyphenyl)pyrylium perchlorate

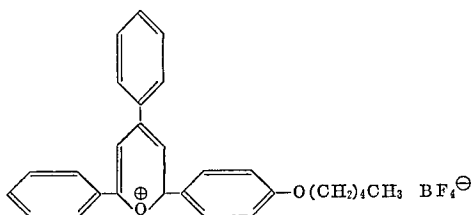


This dye was evaluated by the procedure described in above Example 1 and found to be an excellent electron

acceptor and spectral sensitizer for fogged direct positive photographic emulsions with spectral sensitization extended to 590 m μ with a peak at 520 m μ .

EXAMPLE 3

2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium fluoroborate

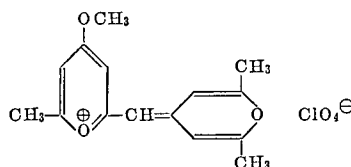
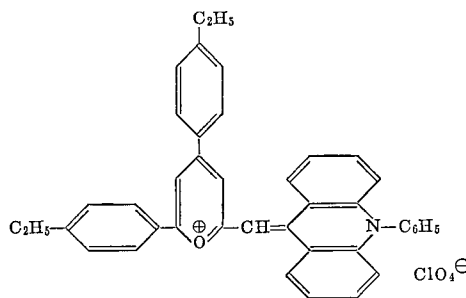


This dye compound as evaluated by the exact procedure described in Example 1 is also an excellent electron acceptor and spectral sensitizer for fogged direct positive photographic emulsions with spectral sensitization extended to 580 m μ with a peak at 500 m μ .

A number of other pyrylium, thiapyrylium and selenapyrylium dye compounds of Formula I above were also tested for reversal properties by the technique described in above Example 1. The results are summarized in Table 1 below. The relative effectiveness of each dye is indicated by a number ranging from 1 to 5, with 1 being least effective and 5 being the best or most effective rating. On this scale, 0 (zero) would indicate no spectral sensitization. The region of spectral sensitization is also listed for each dye.

TABLE 1

Compound	Region of spectral sensitization (m μ)	Relative effectiveness
Example number:		
4..... 2-(4-phenylbutadienyl)-4,6-diphenylpyrylium perchlorate.....	490-640	4
5..... 6-(4-phenylbutadienyl)-2,4-diphenylthiapyrylium perchlorate.....	480-720	4
6..... 2,4-bis-(p-ethoxyphenyl)-6-(p-n-amyloxystyryl)pyrylium fluoroborate.....	480-680	2
7..... 2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium perchlorate.....	480-640	3
8..... 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)pyrylium perchlorate.....	400-560	5
9..... 2,6-bis-(p-anisyl)-4-phenylthiapyrylium fluoroborate.....	480-520	1
10..... 2,6-bis-(p-ethylphenyl)-4-phenylthiapyrylium perchlorate.....	460-530	1
11..... 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)thiapyrylium perchlorate.....	460-600	5
12..... 2,6-diphenyl-4-(p-anisyl)-thiapyrylium chloride.....	460-590	4
13..... 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)-pyrylium fluoroborate.....	360-550	5
14..... 2-(4-phenyl-3-methylbutadienyl)-4,6-diphenylpyrylium perchlorate.....	380-550	3
15..... 2,6-bis-(p-anisyl)-4-(p-n-amyloxyphenyl)thiapyrylium perchlorate.....	405-640	5+
16..... 2,4-diphenyl-6-styrylpyrylium perchlorate.....	430-600	4
17..... 2,4-diphenyl-6-(p-n-amyloxystyryl)pyrylium perchlorate.....	500-720	2
18..... 2,6-diphenyl-4-(p-azidophenyl)pyrylium perchlorate.....	530-630	3
19..... 2,6-bis-(p-anisyl)-4-phenylthiapyrylium fluoroborate.....	450-630	5
20..... 2,6-diphenyl-4-(p-anisyl)pyrylium perchlorate.....	420-530	2
21..... 2,6-diphenyl-4-(p-anisyl)-thiapyrylium fluoroborate.....	460-580	1
22..... 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)pyrylium perchlorate.....	380-560	5
23..... 2,4,6-tris-(p-anisyl)pyrylium fluoroborate.....	420-580	5
24..... 2-(N-phenylacridanylidene)methyl)-4,6-bis-(p-ethylphenyl)-pyrylium perchlorate.....	460-490	1
25..... 2-[p-(β -hydroxyethoxy)phenyl]-4,6-diphenylpyrylium perchlorate.....	420-580	5
26..... 2,6-bis-(p-carboxymethoxyphenyl)-4-phenylpyrylium fluoroborate.....	420-580	3
27..... 2,4,6-triphenylselenapyrylium fluoroborate.....	420-540	1
28..... 2,6-dimethyl-4-methoxypyrylium perchlorate.....	360-520	2
29..... 2,6-bis-(p-n-amyloxyphenyl)-4-(p-anisyl)thiapyrylium chloride.....	440-600	3
30..... 2,4,6-tris-(p-anisyl)thiapyrylium p-toluenesulfonate.....	400-620	5
31..... 2,4,6-tris-(p-anisyl)thiapyrylium sulfoacetate.....	400-620	5
32..... 2,4-bis-(p-anisyl)-6-(p-methoxystyryl)pyrylium sulfoacetate.....	500-560	1
33..... 4-methoxy-6-methyl pyrylo-2-(2,6-dimethyl pyrylo-4-methine-cyanine) perchlorate.....	490-540	2
34..... 2,6-bis-(p-chloromethoxycarbonylphenyl)-4-phenylpyrylium fluoroborate.....	400-580	5
35..... 2,4-bis-(p-ethylphenyl)-6-(p-styrylstyryl)pyrylium perchlorate.....	490-700	2
36..... 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)thiapyrylium fluoroborate.....	420-600	5
37..... 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)thiapyrylium fluoroborate.....	440-600	4
38..... 2,6-diphenyl-4-(p-anisyl)-pyrylium perchlorate.....	420-530	3
39..... 2,6-diphenyl-4-(p-anisyl)-thiapyrylium perchlorate.....	440-580	4



Compound	Region of spectral sensitization (m μ)	Relative effectiveness
40..... 2,6-bis-(p-anisyl)-4-phenylpyrylium perchlorate.....	440-600	5
41..... 2,4,6-tris-(p-anisyl)pyrylium perchlorate.....	400-580	5
42..... 2,4,6-tris-(p-anisyl)thiapyrylium perchlorate.....	400-640	5
43..... 2,6-bis-(p-ethylphenyl)-4-phenylpyrylium perchlorate.....	460-530	1
44..... 2,6-diphenyl-4-(p-acetaminophenyl)pyrylium perchlorate.....	410-560	4
45..... 2,6-diphenyl-4-(o-anisyl)thiapyrylium perchlorate.....	410-560	1
46..... 2-[p-(β -hydroxyethoxy)phenyl]-4-phenyl-6-(p-anisyl)pyrylium perchlorate.....	420-580	5
47..... 2-(2-naphthyl)-4,6-diphenylthiapyrylium perchlorate.....	420-620	5
48..... 2,6-bis-p-biphenyl-4-phenylpyrylium fluoroborate.....	480-580	3
49..... 2,6-diphenyl-4-(p-aminophenyl)thiapyrylium perchlorate.....	420-640	3
50..... 2,6-bis-(p-tolyl)-4-(p-anisyl)pyrylium fluoroborate.....	420-560	5
51..... 2,6-bis-(p-tolyl)-4-(p-anisyl)thiapyrylium chloride.....	460-540	2
52..... 2-[p-(β -hydroxyethoxy)phenyl]-4-phenyl-6-(p-anisyl)thiapyrylium chloride.....	420-600	4
53..... 2,6-bis-(p-n-amylxyphenyl)-4-(p-anisyl)pyrylium perchlorate.....	480-580	3
54..... 2,6-bis-p-biphenyl-4-phenylthiapyrylium chloride.....	440-630	4
55..... 2,4,6-tris-(p-anisyl)thiapyrylium trifluoroacetate.....	420-630	5
56..... 2-methyl-4,6-bis-(p-anisyl)pyrylium sulfoacetate.....	410-560	5
57..... 2,6-bis-(p-methoxystyryl)-4-phenylpyrylium perchlorate.....	500-680	3
58..... 2,6-bis-(p-anisyl)-4-(p-n-amylxyphenyl)thiapyrylium fluoroborate.....	410-640	5

The following examples illustrate the preparation of a photographic element and a reversal image with the novel direct positive emulsions of the invention.

EXAMPLE 59

To 9.0 pounds of a silver chloride gelatin emulsion containing an equivalent of 100 grams of silver nitrate is added 0.017 gram of the dye of Example 1. The emulsion is coated on a non-glossy paper support, and is flashed with white light to give a density of 1.2 when developed in the following developer, diluted 1 part to 2 parts of water:

N-methyl-p-aminophenol sulfate.....	G. 3.1
Sodium sulfite, des.	45
Hydroquinone.....	12
Sodium carbonate, des.	67.5
Potassium bromide.....	1.9
Water to 1 liter.	

The light fogged material can be exposed to an image with light modulated by a Wratten No. 15 filter to give a direct positive image. Similar results are obtained when the dye of Example 2 is substituted for that of Example 1.

EXAMPLE 60

Seven pounds of a silver chloride gelatin emulsion containing the equivalent of 100 g. of silver nitrate is heated to 40° C. and the pH is adjusted to 7.8. Eight cc. of full strength (40%) formalin solution is added and the emulsion is held at 40° C. for 10 minutes. At the end of the holding period, the pH is adjusted to 6.0 and 0.125 g. of the dye of Example 3 added. The emulsion is coated on a support, and provides good direct positive images. Similar results are obtained when the dye of Example 8 is substituted for that of Example 3.

The following examples show various pyrylium compounds as desensitizers in reduction sensitized silver halide emulsions.

EXAMPLES 61-63

A fine grain silver bromide emulsion was reduction sensitized with 10 mg. stannous chloride and divided into several portions. To separate portions of the emulsions were added 0.2 grams, respectively, of the following pyrylium compounds: 2-[α -ethyl- β , β -bis(4-dimethylaminophenyl)vinylene]-4,6-diphenylpyrylium fluoroborate (Compound A); 2-(3,4-diethoxystyryl)-4,6-diphenylthiapyrylium perchlorate (Compound B) and 2,4-diphenyl-6-(1-ethyl-4-p-dimethylaminophenyl-1,3-butadienyl)pyrylium fluoroborate (Compound C). The emulsions were coated on a cellulose acetate film support, chill set, and dried. The films were sensitometrically exposed to a tungsten source modulated by a continuous wedge, and by Wratten filter No. 35 plus No. 38A, No. 16, No. 16, No. 29, and No. 61 plus No. 16. These filters are described in "Kodak Wratten Filters for Scientific

and Technical Use," twenty-second printing, 1966. The films were processed for 5 minutes in a developer having the following composition:

Stock solution

25 Water, about 125° F. (50° C.)—500 cc.
N-methyl-p-aminophenol sulfate—2.5 grams
Sodium sulfite, desiccated—30.0 grams
Hydroquinone—2.5 grams
Sodium metaborate—10.0 grams
30 Potassium bromide—0.5 gram
Phenidone—0.2 gram
Triethylenetetramine—0.2 gram
Water to make 1.0 liter

The results are shown below:

Pyrylium compound	Density in unexposed areas	Minimum density in exposed areas
None—control.....	1.6	(1)
Compound:		
A.....	1.36	.28
B.....	1.06	.16
C.....	1.09	.72

¹ No reversal.

EXAMPLES 64-77

Several other pyrylium dyes were tested by the evaluation procedure described in Example 1, and were found to be effective spectral sensitizers for direct positive emulsions. They are listed below:

Dye
50 Example:
64..... 2,6-diphenyl-4-(4-dipropylaminophenyl)-pyrylium perchlorate.
65..... 2,4,6-tris(4-pentyloxyphenyl)pyrylium perchlorate (sensitizing maximum, 485 m μ).
66..... 4-[4-(N,N-bis- β -chloroethylamino)phenyl]-2,6-diphenylpyrylium perchlorate (sensitizing maximum, 570 m μ).
67..... 2,4-diphenyl-6-(β -ethyl-p-methoxystyryl)-pyrylium fluoroborate (sensitizing maximum, 550 m μ).
68..... 4-(p-n-amylxyphenyl)-2,6-di-(p-methoxyphenyl)-pyrylium perchlorate.
69..... 4-(4-diethylamino-2-ethoxyphenyl)-2,6-diphenylpyrylium perchlorate.
70..... 4-(2-chloro-4-diethylaminophenyl)-2,6-diphenylpyrylium perchlorate.
71..... 4-[4-N,N-di(2-chloroethyl)aminophenyl]-2-(4-methoxyphenyl)-6-phenylpyrylium perchlorate (sensitizing maximum, 550 m μ).
72..... 4-N,N-di(2-chloroethyl)amino-2-methylphenyl-2,6-diphenylpyrylium perchlorate (sensitizing maximum, 575 m μ).
73..... 4-[4-(N- β -chloroethyl-N-ethylamino)phenyl]-2,6-diphenylpyrylium perchlorate (sensitizing maximum, 580 m μ).
74..... 4-(4-dibenzylaminophenyl)-2,6-diphenylpyrylium perchlorate (sensitizing maximum, 580 m μ).
75..... 4-(4-N-allyl-N-methylaminophenyl)-2,6-diphenylpyrylium perchlorate (sensitizing maximum, 580 m μ).
76..... 4-[4-di(2-chloroethyl)amino-2-methylphenyl]-2,6-diphenylthiapyrylium perchlorate (sensitizing maximum 650 m μ).
77..... 4-[4-(N-ethyl-N-2-phthalimidoethylamino)-phenyl]-2,6-diphenylpyrylium perchlorate (sensitizing maximum 575 m μ).
78..... 4-[2-1-methyl-2-phenyl-3-indolyl] 1 benzopyrylium perchlorate.
79..... 4-[2-(1-methyl-2-phenyl-3-indolyl) vinyl]-2-phenylnaphtho[1,2-b]pyrylium bromide.

By substituting other dye compounds of the invention, as defined in Formula I above, into the procedure of the above examples generally similar fogged, direct positive photographic silver halide emulsions and photographic elements may be prepared.

The photographic silver halide emulsion and other layers present in the photographic elements made according to the invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde, and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy starch or oxy plant gums, and the like. The emulsion layers can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including, for example, lubricating materials, stabilizers, speed increasing materials, absorbing dyes, plasticizers, and the like. These photographic emulsions can also contain in some cases additional spectral sensitizing dyes. Furthermore, these emulsions can contain color forming couplers or can be developed in solutions containing couplers or other color generating materials. Among the useful color formers are the monomeric and polymeric color formers, e.g. pyrazolone color formers, as well as phenolic, heterocyclic and open chain couplers having a reactive methylene group. The color forming couplers can be incorporated into the direct positive photographic silver halide emulsion using any suitable technique, e.g., techniques of the type shown in Jelley et al. U.S. Pat. 2,322,027, issued June 15, 1943, Fierke et al. U.S. Pat. 2,801,171, issued July 30, 1957, Fisher U.S. Pats. 1,055,155 and 1,102,028, issued Mar. 4, 1913 and June 30, 1914, respectively, and Wilmanns U.S. Pat. 2,186,849 issued Jan. 9, 1940. They can also be developed using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones, and the like.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

I claim:

1. A fogged direct positive, photographic silver halide emulsion containing at least one dye compound selected from the group consisting of a pyrylium salt and a thiapyrylium salt.

2. A direct positive emulsion of claim 1 wherein said dye compound is a pyrylium salt.

3. A direct positive emulsion of claim 1 wherein said dye compound is a thiapyrylium salt.

4. A direct positive emulsion of claim 1 in which said silver halide is present in the form of chemically fogged silver halide grains.

5. A direct positive emulsion of claim 1 in which said silver halide is present in the form of reduction and gold salt fogged silver halide grains.

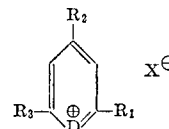
6. A direct positive emulsion of claim 1 containing a photographic color former.

7. A direct positive, photographic emulsion in accordance with claim 1 which comprises fogged silver halide grains, said grains being such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about 1 upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

potassium cyanide—50 mg.
acetic acid (glacial)—3.47 cc.
sodium acetate—11.49 g.
potassium bromide—119 mg.
water to 1 liter.

8. A direct positive emulsion in accordance with claim 1 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a size which is within about 40% of the average grain size.

9. A fogged direct positive photographic silver halide emulsion containing a dye compound selected from those represented by the following general formula:



wherein D represents a member selected from the group consisting of an oxygen atom and a sulfur atom, X represents an acid anion, and R₁, R₂ and R₃ each represents a member selected from the group consisting of an alkyl group, an alkoxy group, an aryl group, and an alkenyl group.

10. A direct positive emulsion of claim 9 wherein said dye compound is a pyrylium salt.

11. A direct positive emulsion in accordance with claim 1 which comprises a thiapyrylium salt, at least 95%, by weight, of said grains having a size which is within about 40% of the average grain size.

12. A direct positive emulsion of claim 9 in which said silver halide is present in the form of chemically fogged silver halide grains.

13. A direct positive emulsion of claim 9 in which said silver halide is present in the form of reduction and gold fogged silver halide grains.

14. A direct positive, photographic emulsion in accordance with claim 9 which comprises fogged silver halide grains, said grains being such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least about 1 upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Kodak DK-50 developer after being bleached for about 10 minutes at about 68° F. in a bleach composition of:

potassium cyanide—50 mg.
acetic acid (glacial)—3.47 cc.
sodium acetate—11.49 g.
potassium bromide—119 mg.
water to 1 liter.

15. A direct positive, photographic emulsion in accordance with claim 9 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having a size which is within about 40% of the average grain size.

16. A fogged direct positive photographic silver halide emulsion containing a dye compound selected from the group consisting of

a 2,6-di-p-methoxyphenyl-4-phenyl pyrylium salt;
a 2,6-bis-(p-anisyl)-4-(p-n-amyloxyphenyl)pyrylium salt;
a 2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium salt;
a 2-(4-phenylbutadienyl)-4,6-diphenylpyrylium salt;
a 2,4-diphenyl-6-(4-phenylbutadienyl)thiapyrylium salt;
a 2,4-bis-(p-ethoxyphenyl)-6-(p-n-amyloxystyryl) pyrylium salt;
a 2-(p-n-amyloxyphenyl)-4,6-diphenylpyrylium salt;
a 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)pyrylium salt;
a 2,6-bis-(p-anisyl)-4-phenylthiapyrylium salt;
a 2,6-bis-(p-ethylphenyl)-4-phenylthiapyrylium salt;
a 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)thiapyrylium salt;
a 2,6-diphenyl-4-(p-anisyl)thiapyrylium salt;
a 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)pyrylium salt;
a 2-(4-phenyl-3-methylbutadienyl)-4,6-diphenylpyrylium salt;

- a 2,6-bis-(p-anisyl)-4-(p-n-amyloxyphenyl)thiapyrylium salt;
 a 2,4-diphenyl-6-styrylpyrylium salt;
 a 2,4-diphenyl-6-(p-n-amyloxystyryl)pyrylium salt;
 a 2,6-diphenyl-4-(p-azidophenyl)pyrylium salt;
 a 2,6-bis-(p-anisyl)-4-phenylthiapyrylium salt;
 a 2,6-diphenyl-4-(p-anisyl)pyrylium salt;
 a 2,6-diphenyl-4-(p-anisyl)thiapyrylium salt;
 a 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)pyrylium salt;
 a 2,4,6-tris-(p-anisyl)pyrylium salt;
 a 2-(N-phenylacridanylidene)methyl-4,6-bis-(p-ethylphenyl)pyrylium salt;
 a 2-[p-(β -hydroxyethoxy)phenyl]-4,6-diphenylpyrylium salt;
 a 2,6-bis-(p-carboxymethoxyphenyl)-4-phenylpyrylium salt;
 a 2,4,6-triphenylselenapyrylium salt;
 a 2,6-dimethyl-4-methoxyppyrylium salt;
 a 2,6-bis-(p-n-amyloxyphenyl)-4-(p-anisyl)thiapyrylium salt;
 a 2,4,6-tris-(p-anisyl)pyrylium salt;
 a 2,4,6-tris-(p-anisyl)thiapyrylium salt;
 a 2,4-bis-(p-anisyl)-6-(p-methoxystyryl)pyrylium salt;
 a 4-methoxy-6-methyl pyrylo-2-(2,6-dimethyl pyrylo-4-methinecyanine) salt;
 a 2,6-bis-(p-chloromethoxycarbonylphenyl)-4-phenylpyrylium salt;
 a 2,4-bis-(p-ethylphenyl)-6-(p-styrylstyryl)pyrylium salt;
 a 2,6-bis-(p-ethylphenyl)-4-(p-n-amyloxyphenyl)thiapyrylium salt;
 a 2,6-bis-(p-ethylphenyl)-4-(p-anisyl)thiapyrylium salt;
 a 2,6-diphenyl-4-(p-anisyl)pyrylium salt;
 a 2,6-diphenyl-4-(p-anisyl)thiapyrylium salt;
 a 2,6-bis-(p-anisyl)pyrylium salt;
 a 2,4,6-tris-(p-anisyl)pyrylium salt;
 a 2,4,6-tris-(p-anisyl)thiapyrylium salt;
 a 2,6-bis-(p-ethylphenyl)-4-phenylpyrylium salt;
 a 2,6-diphenyl-4-(p-acetaminophenyl)pyrylium salt;
 a 2,6-diphenyl-4-(o-anisyl)thiapyrylium salt;
 a 2-[p-(β -hydroxyethoxy)phenyl]-4-phenyl-6-(p-anisyl)pyrylium salt;
 a 2-(2-naphthyl)-4,6-diphenylthiapyrylium salt;
 a 2,6-bis-(p-biphenyl)-4-phenylpyrylium salt;
 a 2,6-diphenyl-4-(p-aminophenyl)thiapyrylium salt;
 a 2,6-bis-(p-tolyl)-4-(p-anisyl)pyrylium salt;
 a 2,6-bis-(p-tolyl)-4-(p-anisyl)thiapyrylium salt;
 a 2-[p-(β -hydroxyethoxy)phenyl]-4-phenyl-6-(p-anisyl)thiapyrylium salt;
 a 2,6-bis-(p-n-amyloxyphenyl)-4-(p-anisyl)pyrylium salt;
 a 2,6-bis-(p-biphenyl)-4-phenylthiapyrylium salt;
 a 2,4,6-tris-(p-anisyl)thiapyrylium salt;
 a 2-methyl-4,6-bis-(p-anisyl)pyrylium salt;
 a 2,6-bis-(p-methoxystyryl)-4-phenylpyrylium salt;
 a 2,6-bis-(p-anisyl)-4-(p-n-amyloxyphenyl)thiapyrylium salt;
 a 2,6-diphenyl-4-(4-dipropylaminophenyl)pyrylium salt;
 a 2,4,6-tris(4-pentyloxyphenyl)pyrylium salt;
 a 4-[4-(N,N-bis- β -chloroethylamino)phenyl]-2,6-diphenylpyrylium salt;
 a 2,4-diphenyl-6-(β -ethyl-p-mehoxystyryl)pyrylium salt;

- a 4-(p-n-amyloxyphenyl)-2,6-di-(p-mehoxyphenyl)pyrylium salt;
 a 4-(4-diethylamino-2-ethoxyphenyl)-2,6-diphenylpyrylium salt;
 5 a 4-(2-chloro-4-diethylaminophenyl)-2,6-diphenylpyrylium salt;
 a 4-[4-N,N-di(2-chloroethyl)aminophenyl]-2-(4-methoxyphenyl)-6-phenylpyrylium salt;
 a 4-[4-N,N-di(2-chloroethyl)amino-2-methylphenyl]-2,6-diphenylpyrylium salt;
 10 a 4-[4-(N- β -chloroethyl-N-ethylamino)phenyl]-2,6-diphenylpyrylium salt;
 a 4-(4-dibenzylaminophenyl)-2,6-diphenylpyrylium salt;
 a 4-(4,N-allyl-N-methylaminophenyl)-2,6-diphenylpyrylium salt;
 15 a 4-[4-di-(2-chloroethyl)amino-2-methyl-phenyl]-2,6-diphenylthiapyrylium salt and
 a 4-[4-(N-ethyl-N,2-phthalimidoethylamino)-phenyl]-2,6-diphenylpyrylium salt.
 20 17. A direct positive, photographic emulsion in accordance with claim 16 which comprises fogged silver halide grains, said grains being such that a test portion thereof, when coated as a photographic silver halide emulsion on a support to give a maximum density of at least
 25 about 1 upon processing for 6 minutes at about 68° F. in Kodak DK-50 developer, has a maximum density which is at least about 30% greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Kodak DK-50 developer
 30 after being bleached for about 10 minutes at about 68° F. in a bleach composition of:
 potassium cyanide—50 mg.
 acetic acid (glacial)—3.47 cc.
 sodium acetate—11.49 g.
 35 potassium bromide—119 mg.
 water to 1 liter
 18. A direct positive, photographic emulsion in accordance with claim 16 which comprises fogged silver halide grains, at least 95%, by weight, of said grains having
 40 a size which is within about 40% of the average grain size.
 19. A photographic element comprising a support coated with at least one layer containing a direct positive photographic emulsion of claim 1.

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