

[54] **DIRECT-POSITIVE PHOTOGRAPHIC ELEMENTS CONTAINING MULTIPLE LAYERS**

[72] Inventors: Robert C. Taber; James E. Koller, both of Rochester, N.Y.

[73] Assignee: Eastman Kodak Company, Rochester, N.Y.

[22] Filed: Aug. 14, 1969

[21] Appl. No.: 850,197

[52] U.S. Cl. .... 96/68, 96/67, 96/64

[51] Int. Cl. .... G03c 1/76

[58] Field of Search .... 96/68, 64, 67

[56] **References Cited**

**UNITED STATES PATENTS**

1,905,188	4/1933	Sease.....	96/68
2,566,180	8/1951	Fallesen.....	96/56

3,178,282	4/1965	Luckey.....	96/64
3,352,672	11/1967	Hoppe.....	96/64
3,450,536	6/1969	Wyckoff.....	96/68
3,457,072	7/1969	Ditzer.....	96/68
3,471,295	10/1969	Bockly.....	96/64

Primary Examiner—Norman G. Torchin

Assistant Examiner—Judson R. Hightower

Attorney—W. H. J. Kline, Bernard D. Wiese and Gerald E. Battist

[57] **ABSTRACT**

This invention relates to direct-positive silver halide elements comprising (1) duplicate layers containing silver halide emulsions having substantially the same light-response characteristics and (2) means for providing a sensitivity difference between said duplicate layers of at least 0.5 log exposure. In certain preferred embodiments, relatively light-insensitive absorbing silver halide emulsions and/or light-absorbing dyes are used in an interlayer to provide an effective density of 0.1 to 1.5.

**16 Claims, 3 Drawing Figures**

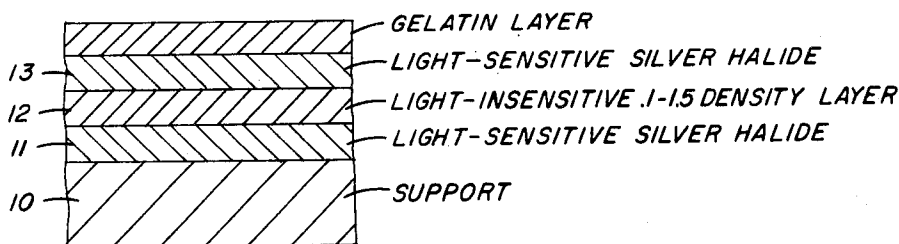


FIG. 1

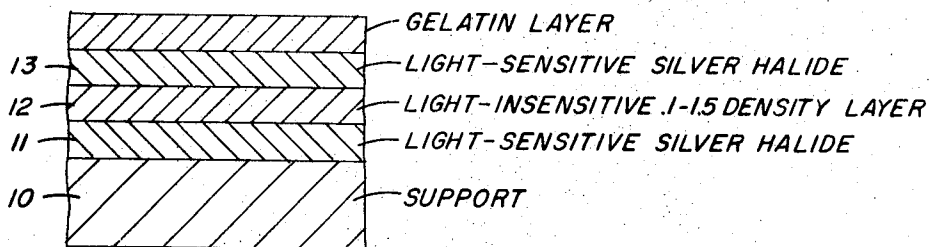


FIG. 2

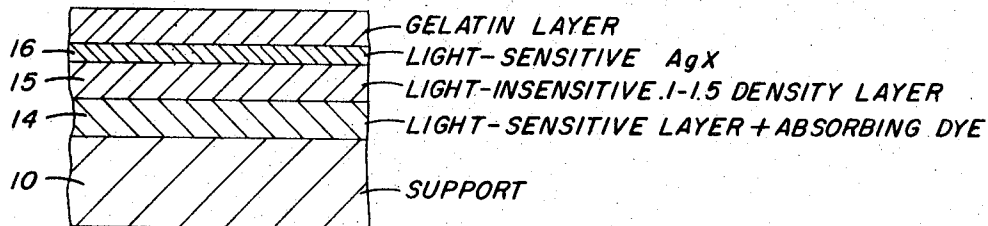
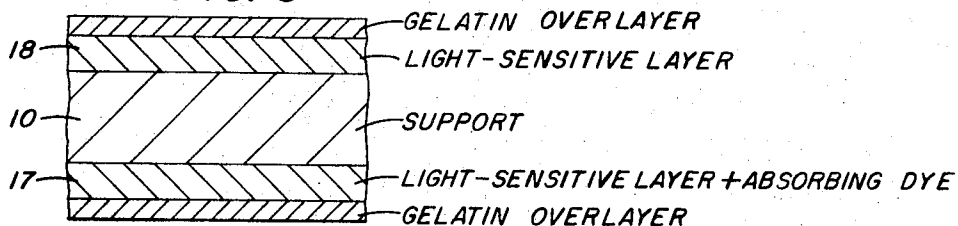


FIG. 3



ROBERT C. TABER  
JAMES E. KOLLER  
INVENTORS

BY

*Gerald Battist*

ATTORNEY

## DIRECT-POSITIVE PHOTOGRAPHIC ELEMENTS CONTAINING MULTIPLE LAYERS

This invention relates to photographic elements. In one aspect, this invention relates to direct-positive silver halide elements having low-contrast, extended latitude, photographic characteristics. In another aspect, this invention relates to direct-positive photographic elements having duplicate light-sensitive layers with a light-insensitive layer having a density of about 0.1 to about 1.5 interposed between said duplicate layers.

It is known in the art that extended latitude negative photographic elements can be provided by utilizing several layers of emulsions of different sensitivity. Moreover, it is known that extended latitude direct-positive elements can be made with direct-positive emulsions having different sensitivity characteristics such as, for example, by using emulsions of different grain size or emulsions containing grains which have been fogged to different fog levels. However, in commercial production it is desirable to have improved and simple methods of making extended latitude direct-positive elements which will provide an exposure curve of substantially the same shape without wide variance in exposure response from batch to batch and from start to finish on a given coating run.

We have now discovered improved layer arrangements for direct-positive photographic elements whereby extended latitude may be obtained with very good reproducibility of exposure vs. density curves. Generally, the photographic elements of this invention comprise at least two layers of direct-positive silver halide emulsions having similar sensitivity characteristics, i.e., duplicate layers, and means for providing a reduced exposure in one of said layers.

In one embodiment, the direct-positive emulsions used in each of the duplicate layers are prepared as one emulsion and merely coated as two separate layers.

In a preferred embodiment of this invention, the direct-positive element comprises at least two layers containing direct-positive emulsions having similar sensitivity characteristics and a substantially light-insensitive interlayer having an effective density of 0.1 to 1.5, and preferably 0.3 to 0.7, interposed between said layers.

In another preferred embodiment, the duplicate layers contain blends of direct-positive emulsions.

In yet another embodiment, absorbing dyes are incorporated in the direct-positive emulsion layers closest to the support. In one variation of this embodiment, the furthestmost direct-positive layers from the support have a higher silver-to-vehicle ratio and are at least 50 percent thinner coatings than at least one of the corresponding light-sensitive underlayers.

According to the various embodiments of the invention, an extended latitude photographic direct-positive silver halide element can be provided repetitively with exposure curves of similar shape with very little variance at any point on the average curve; this can be obtained with fewer requisite separate emulsions for each element. Moreover, the duplicate emulsion layers can be coated on the same side of the support to obtain better image sharpness as the layers are in closer proximity.

FIGS. 1 and 2 generally represent two preferred embodiments according to this invention.

The support 10 is generally any photographic film base such as cellulose acetates, polyesters, polycarbonates, paper, etc., which can be subbed or coated before the photographic emulsions are coated thereon. The light-sensitive layers 11 and 13 can be direct-positive, light-sensitive layers which can have substantially the same sensitivity characteristics including blends of direct-positive emulsions. The interlayer 12 is substantially light-insensitive and has an effective density of 0.1 to about 1.5 and preferably 0.3-0.7 to reduce the exposure on the underlayer 11. The effective density is understood to mean that it is effective in reducing the light exposure over the region of sensitivity of the underlayer 11. The interlayers having this effective density will, of course, transmit between about 3 to about 75 percent of the radiant energy reaching the inter-

layer. FIG. 3 represents one embodiment of the invention wherein the silver halide layers 17 and 18 are coated on opposite sides of the support and one of the layers, such as layer 17, contains an absorbing dye.

In one preferred embodiment according to FIG 2, an absorbing dye is incorporated in the underlayer 14 having an effective absorption in the region of light sensitivity of the emulsion in layer 14. Preferably the light-sensitive emulsion layer 16 in this arrangement is about 50 percent thinner than emulsion layer 14 and it has a higher silver-to-gelatin ratio. The layer 15, which is a 0.1-1.5 density layer, is preferably included in this embodiment to provide exceptional extended latitude properties; however, it can also be omitted and still provide extended latitude characteristics as the absorbing dye will somewhat reduce the effective exposure of layer 14.

In a preferred embodiment, the direct-positive compositions of this invention are blue-sensitive compositions. It is understood that blue-sensitive means that the direct-positive compositions will provide a reversal image when exposed with light in the 350- to 500-millimicron range of the electromagnetic spectrum. The silver halide compositions can also be spectrally sensitized to form reversal images when exposed in others regions of the spectrum such as in the green and red regions. However, they all have the property of being capable of forming a reversal image when exposed with light in the blue region of the visible spectrum. Generally, these emulsions have high photographic speed compared to compositions such as conventional Herschel reversal emulsions. Typical useful elements containing the emulsions of the invention may also be exposed with UV light and may be exposed from the front or back, depending on the contrast desired.

Typical direct-positive silver halide compositions which can be characterized by the above tests and which are useful in this invention are: (1) emulsions comprising silver halide grains having internal centers which promote the deposition of photolytic silver and an outer region or shell of a fogged insoluble silver salt and preferably a halogen-conducting compound in said emulsion or (2) an emulsion which comprises fogged silver halide grains and an organic compound which accepts electrons, 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 0.5 upon processing for 5 minutes at about 68° F. in Developer A, has a maximum density which is at least about 30 percent greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Developer A 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

Developer A has the composition:

N-methyl-p-aminophenol sulfate	2.5 g.
sodium sulfite (anhydrous)	30.0 g.
hydroquinone	2.5 g.
sodium metaborate	10.0 g.
potassium bromide	0.5 g.
water to	1.0 liter

This invention can be practiced with 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. These emulsions can be prepared in various ways, such as those described in Berriman, U.S. Pat. No. 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 B 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 B

N-methyl-p-aminophenol sulfate	2.5 g.
ascorbic acid	10.0 g.
potassium metaborate	35.0 g.
potassium bromide	1.0 g.
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 in the Berriman patent referred to above. Silver salt cores containing centers attributable to a metal of Group VIII of the Periodic Table, e.g., palladium, iridium or platinum and the like, are especially useful since these centers also appear to function as electron acceptors. Chemical sensitization techniques of the type described by Antoine Hautot and Henri Saubienier in *Science et Industries Photographiques*, Vol. XX-VIII, Jan. 1957, pages 1 to 23, and Jan. 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.

In another embodiment, the silver halide emulsions can comprise silver halide grains having centers which promote the deposition of photolytic silver which are either sufficiently small or sufficiently buried within the crystal as to be not accessible to initiate development to a visible image. Silver halide grains of this type can be provided by either using very low concentrations of the sensitizing agent throughout the precipitation or adding the sensitizing agent to the precipitation medium during the initial part of the precipitation whereby the concentration of the sensitizing agent will be lowered significantly by occlusion of the agent in the grains so that continued precipitation would result in lowered concentration of centers for promoting deposition of photolytic silver in the outer regions of each grain.

The practice of this invention is particularly suitable for high-speed direct-positive emulsions comprising fogged silver halide grains and a compound which accepts electrons, as described in U.S. Pat. No. 3,501,306 of Illingsworth. 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 1 upon processing for 6 minutes at about 68° F. in Developer A, has a maximum density which is at least about 30 percent greater than the maximum density of an identical coated test portion which is processed for 6 minutes at about 68° F. in Developer A 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 percent and generally at least about 40 percent of their fog when bleached for 10 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 6 minutes at about 68° F. in Developer A and comparing the density of such a coating with an identical coating which is processed for 6 minutes at 68° F. in Developer A 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 percent greater, generally at least 60 percent greater, than the maximum density of the bleached coating.

The silver halides employed in the preparation of the photographic emulsions include silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chlorobromiodide, and the like. Preferably the halide comprises at least 50 percent bromide and/or less than 10 percent iodide. Emulsion blends, e.g., blends of silver chloride and silver chlorobromide, can be used. Also, the core of the silver halide grain can be composed of silver halide of different composition than that in the outer shell of the grain.

Silver halide grains having an average grain size less than about 2 microns, 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 in U.S. Pat. No. 3,501,305 of Illingsworth. Such grains advantageously have a rather uniform diameter frequency distribution, as described and claimed in U.S. Pat. No. 3,501,307 of Illingsworth. For example, at least 95 percent, by weight, of the photographic silver halide grains can have a diameter which is within about plus or minus 40 percent, preferably within about plus or minus 30 percent, of the mean grain size. 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, and "Methods of Particle-Size Analysis," *ASTM Symposium on Light Microscopy*, by Loveland, 1953, pages 94-122. 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 5 minutes at 68° F. in Developer A when such an emulsion is coated at a coverage of 50 to about 500 mg. of silver per square foot of support. The photographic silver halides can be coated at silver coverages in the range of about 50 to 500 milligrams of silver per square foot.

In preferred embodiments of this invention, electron acceptors and halogen conductors (sometimes referred to as halogen acceptors) are present in the direct-positive emulsions. When the grains of the silver halide emulsion are substantially free of internal sites for the deposition of photolytic silver, it is essential that an electron acceptor be present in the emulsion if it is to be reversed by blue light.

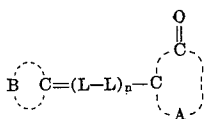
The electron acceptors or halogen conductors which give particularly good results in the practice of this invention can be characterized in terms of their polarographic halfwave potentials, i.e., their oxidation reduction potentials determined by polarography. The electron acceptors useful herein have an anodic polarographic potential and a cathodic polarographic potential which, when added together, give a positive sum. The halogen conductors useful herein have an anodic polarographic potential less than 0.85 and a cathodic polarographic potential which is more negative than -1.0. Preferred halogen conductors have an anodic polarographic potential less than 0.62 and a cathodic polarographic potential which is

more negative than  $-1.3$ . Cathodic measurements can be made with a  $1 \times 10^{-4}$  molar solution of the electron acceptor in a solvent, for example, methanol which is  $0.05$  molar in lithium chloride using a dropping mercury electrode with the polarographic halfwave potential for the most positive cathodic wave being designated  $E_c$ . Anodic measurements can be made with  $1 \times 10^{-4}$  molar aqueous solvent solution, for example, methanolic solutions of the electron acceptor which are  $0.05$  molar in sodium acetate and  $0.005$  molar in acetic acid using a carbon paste of pyrolytic graphite electrode, with the voltammetric half-peak potential for the most negative anodic response being designated  $E_a$ . In each measurement, the reference electrode can be an aqueous silver-silver chloride (saturated potassium chloride) electrode at  $20^\circ \text{C}$ . Electrochemical measurements of this type are known in the art and are described in *New Instrumental Methods in Electrochemistry*, by Delahay, Interscience Publishers, New York, 1954; *Polarography*, by Kolthoff and Lingane, 2nd Edition, Interscience Publishers, New York, New York, 1952; *Analytical Chemistry*, 36, 2426 (1964) by Elving; and *Analytical Chemistry*, 30, 1576 (1958) by Adams. Signs are given according to IUPAC, Stockholm Convention 1953.

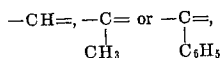
Advantageously, these electron acceptors used herein also provide spectral sensitization such that the ratio of minus blue relative speed to blue relative speed of the emulsion is greater than  $7$ , and preferably greater than  $10$ , when exposed to a tungsten light source through Wratten No. 16 and No. 35 plus 38A filters respectively. Such electron acceptors can be termed "spectrally sensitizing electron acceptors". However, electron acceptors can be used which do not spectrally sensitize the emulsion.

An especially useful class of electron acceptors which can be used in the direct-positive photographic silver halide emulsions and processes of this invention are cyanine dyes, such as the imidazo[4,5-b]quinoxaline dyes. Dyes of this class are described in Brooker and VanLare Belgian Pat. No. 660,253 issued Mar. 15, 1965. In these dyes, the imidazo[4,5-b]quinoxaline nucleus is attached, through the two-carbon atom thereof to the methine chain. Typical good electron-acceptor dyes used in direct-positive emulsions are disclosed in Illingsworth and Spencer, Belgian Pat. No. 695,364 granted Sept. 11, 1967.

A preferred class of halogen-conducting compounds useful in this invention is characterized by an anodic halfwave potential which is less than  $0.62$  and a cathodic halfwave potential which is more negative than  $-1.3$ . A preferred class of halogen conductors that can be used in the practice of this invention comprises the spectral sensitizing merocyanine dyes having the formula:



where A represents the atoms necessary to complete an acid heterocyclic nucleus, e.g., rhodanine, 2-thiohydantoin and the like, B represents the atoms necessary to complete a basic nitrogen-containing heterocyclic nucleus, e.g., benzothiazole, naphthothiazole, benzoxazole and the like, each L represents a methine linkage, e.g.,



and  $n$  is an integer from  $0$  to  $2$ , i.e.,  $0$ ,  $1$  or  $2$ . Typical halogen-conducting compounds are disclosed in Wise, Belgian Pat. No. 695,361 granted Sept. 11, 1967.

In the preparation of the above photographic emulsions, the electron acceptors, halogen conductors, bromide and iodide salts are advantageously incorporated in the washed, finished

silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating such 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 solvents, 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 the electron acceptors and halogen conductors. The type of silver halide emulsions that can be sensitized with these dyes includes 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 ethers, partially hydrolyzed cellulose acetate and the like. The binding agents for the emulsion layer can also contain dispersed polymerized vinyl compounds such as disclosed, for example, in U.S. Pat. No. 3,142,568 by Nottorf issued July 28, 1964, U.S. Pat. No. 3,193,386 by White issued July 6, 1965, U.S. Pat. No. 3,062,674 by Houck et al. issued Nov. 6, 1962, and U.S. Pat. No. 3,220,844 by Houck et al. issued Nov. 30, 1965, and include the water-insoluble polymers and latex copolymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The interlayers useful according to this invention generally contain an adsorbing dye and/or a relatively insensitive silver halide. In one preferred embodiment, when an insensitive silver halide is used in the interlayer, it has a light sensitivity of at least less than one-tenth of one adjacent light-sensitive recording layer. Typical silver halides useful in the interlayer can be made as described in Trivelli and Smith, above, U.S. Pat. No. 3,206,313 by Porter et al. issued Sept. 14, 1965, and U.S. Pat. No. 2,592,250 by Davey et al. issued Apr. 8, 1952. The silver halide interlayers generally contain desensitizing compounds such as described in U.S. Pat. No. 2,954,292 by Duffin et al. issued Sept. 27, 1960, U.S. Pat. No. 2,965,485 by Duffin et al. issued Dec. 20, 1960, U.S. Pat. No. 2,541,472 by Kendall et al. issued Feb. 13, 1951, and U.S. Pat. No. 3,340,063 by Kalenda issued Sept. 5, 1967. The desensitizers are generally utilized in concentrations sufficient to provide a light sensitivity of at least one-tenth or less than that of the recording emulsions in the respective element in which it is to be used.

The absorbing dyes which can be incorporated into the underlayers of the elements according to this invention generally include those dyes described in U.S. Pat. No. 3,253,921 by Sawdey issued May 31, 1966, U.S. Pat. No. 2,274,782 by Gaspar issued Mar. 3, 1942, U.S. Pat. No. 2,527,583 by Silbestein et al. issued Oct. 31, 1950, French Pat. No. 1,359,683 by Heseltine issued Mar. 23, 1964, and U.S. Pat. No. 2,956,879 by VanCampen issued Oct. 18, 1960. If desired, the dyes may be mordanted, for example, as described in U.S. Pat. No. 3,282,699 by Jones et al. issued Nov. 1, 1966. Typical useful absorbing dyes include: anhydro-1,1'-diethyl-2,2'-cyanine hydroxide, monosulfonated; anhydro 9-ethyl-3,3'-dimethyl-4,5,4',5'-dibenzothiacarbocyanine hydroxide, disulfonated; 4-[4-(3-ethyl-2(3H)-benzoxazolyldiene)-2-butenylidene]-3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one, monosulfonated; anhydro-3,3'-diethyl-9-methyl-4,5,4',5'-dibenzothiacarbocyanine hydroxide, disulfonated; 4-[(3-ethyl-2(3H)-benzoxazolyldiene)ethylidene]-3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one, monosulfonated; and anhydro-3,3',9-triethyl-5,5'-di(p-sulfophenyl)oxacarbocyanine hydroxide. When spectrally sensitized direct-positive emulsions are used in the recording layers, an absorbing dye is generally used in the interlayer or the duplicate layer nearer the support to provide an effective reduction in exposure over the area of light sensitivity of the emulsion. Preferably, the dyes used in the interlayer or underlayers are of the non-wandering type or are mordanted in the respective layer. How-

ever, in certain embodiments the absorbing dyes can be incorporated in one layer and allowed to wander into other layers, especially in those embodiments where the outermost light-sensitive layer is thinner than other sensitive layers. Of course, dyes can also be incorporated in each layer at the diffusion equilibrium concentration for constant reproducibility.

The invention can be further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

A direct-positive gelatino emulsion containing silver bromide grains comprising a central core of silver bromide which promote the deposition of photolytic silver and an outer shell comprising fogged silver bromide that develops to silver without exposure is prepared as described in Example 2 of Berriman, U.S. Pat. No. 3,367,778. Said emulsion is then divided into three separate aliquot portions and fogged to different levels with the following gold and reducing agents.

- Emulsion A - 0.10 mg. of thiourea dioxide/silver mole 1.50 mg. of potassium chloroaurate/silver mole
- Emulsion B - 0.20 mg. of thiourea dioxide/silver mole 1.50 mg. of potassium chloroaurate/silver mole
- Emulsion C - 0.40 mg. of thiourea dioxide/silver mole 3.00 mg. of potassium chloroaurate/silver mole

An electron acceptor dye of the type described in Belgian Pat. No. 695,356 is added to the three emulsions along with other beneficial coating addenda dictated by normal image, e.g., spreading agents, hardening agents and the like. The coatings are coated on a polyester film support at a coverage of 100 mg. of silver and 190 mg. of gelatin/ft.<sup>2</sup>. A protective gelatin layer is coated at 83 mg. of gelatin/ft.<sup>2</sup> over the emulsion layer. The three coatings are then exposed for 10 seconds on an Eastman 1B sensitometer and developed for 6 minutes at 70° C. in an Elonhydroquinone developer, fixed and washed. The processed coatings exhibit a direct-positive image with the following results:

Emulsion Number	Relative Speed	Gamma	Dmax	Dmin
A	100	3.82	1.79	0.14
B	246	3.18	1.77	0.14
C	933	2.16	1.82	0.14

The following examples are overcoated with a protective gelatin layer at 83 mg. gelatin/ft.<sup>2</sup>. All the examples are processed in a manner similar to that described in Example 1.

EXAMPLE 2

A blended melt is prepared that comprises 44 percent of Emulsion A, 33 percent of Emulsion B and 23 percent of Emulsion C. An electron acceptor dye is added as described in Example 1 and the emulsion is coated at 120 of mg. of silver/ft.<sup>2</sup>.

EXAMPLE 3

A melt is prepared as described in Example 2 and coated as depicted in FIG. 2 on a 7-mil polyester film support as Emulsion layer 14 at 135 mg. of silver/ft.<sup>2</sup>. To this emulsion layer is added two absorbing dyes: Dye A at 1 mg./ft.<sup>2</sup> and Dye B at 2 mg/ft.<sup>2</sup>. Both absorbing dyes are listed in French Pat. No. 1,359,683 with Dye A described in Example 6 and Dye B described in Example 7.

A substantially light-insensitive silver halide emulsion is prepared similar to that described in Example 1, except the emulsion is not fogged, chemically sensitized or spectrally sensitized, and coated as emulsion layer 15 at 135 mg. silver/ft.<sup>2</sup>.

A third melt is prepared using 100 percent of emulsion A and spectrally sensitized as described in Example 1. The melt is coated as emulsion layer 16 at 60 mg. silver/ft.<sup>2</sup>.

EXAMPLE 4

A photographic duplicating material is prepared similar to that described in Example 3, except emulsion layer 16 contains a spectrally sensitized melt comprising 60 percent of Emulsion A and 40 percent of Emulsion B. The absorbing dyes are coated in emulsion layer 14 at 2 mg./ft.<sup>2</sup> of Dye A and 4 mg./ft.<sup>2</sup> of Dye B. Emulsion layer 14 is coated at 98 mg. of silver/ft.<sup>2</sup>.

The following table clearly indicates that when a multilayer coating of our invention such as Example 3 or 4 is compared to a single layer coating, Example 2, exposure latitude and maximum density of approximately twofold can be obtained. The resulting image of this duplicating material has extremely good quality with respect to sharpness.

Example Number	Dmax	Dmin	Gamma	Exposure Latitude in log E Units
2	1.74	0.14	1.10	1.2
3	2.91	0.14	1.08	2.3
4	3.31	0.18	1.14	2.5

The exposure latitude is determined as the difference between the logarithm of the exposure required to produce a density 0.2 unit above minimum and that required for a density 0.1 unit below maximum.

EXAMPLE 5

A blended melt is prepared that comprises 45 percent of Emulsion A, 30 percent of Emulsion B and 25 percent of Emulsion C of Example 1. The melt is spectrally sensitized as described in Example 1 and coated at 100 mg. of silver/ft.<sup>2</sup> on one side of a support.

EXAMPLE 6

A melt is prepared as described in Example 5 and coated at 100 mg. of silver/ft.<sup>2</sup> on both sides of a support. To one coating is added two absorbing dyes: Dye A, 6 mg./ft.<sup>2</sup>, and Dye B, 12 mg./ft.<sup>2</sup>. Both absorbing dyes are listed in French Pat. No. 1,359,683 with Dye A described in Example 6 and Dye B described in Example 7.

EXAMPLE 7

A solarized direct-positive silver halide emulsion is prepared as described in U.S. Pat. No. 2,184,013 and coated on one side of a support at 440 mg. of silver/ft.<sup>2</sup> with the electron-accepting dye 5-[1-ethoxyethylidene]-3-phenyl rhodanine coated in the emulsion layer at 2 mg./ft.<sup>2</sup>.

EXAMPLE 8

The emulsion melt described in Example 7 is coated on both sides of a support at 440 mg. of silver/ft.<sup>2</sup>. Dyes A and B are added to the emulsion melt on one side of a support and coated at 7 mg./ft.<sup>2</sup> and 9 mg./ft.<sup>2</sup>, respectively.

The following table clearly indicates that when the duplitized coatings, Examples 6 and 8, are compared to respective single-layer coatings, Examples 5 and 7, an exposure latitude of approximately twofold is obtained.

Example Number	Dmax	Gamma	Exposure Latitude in Log E. Units
5	1.74	1.10	1.2
6	3.30	1.06	2.4
7	1.90	1.28	1.1
8	3.68	1.46	2.0

The exposure latitude is determined by the log E units between 0.1 density units below maximum density and 0.2 density units above minimum density.

The following example illustrates another method of changing the characteristic curve in a duplitized emulsion material.

EXAMPLE 9

A blended melt is prepared in a manner similar to that described in Example 5 except the emulsion ratios are 42 percent of Emulsion A, 33 percent of Emulsion B and 25 percent of Emulsion C. The melt is then coated on both sides of a polyester film support as shown in FIG. 3 at the coverages listed in the following table. To the melt for layer 17 is added 4.2 g. of Dye A/silver mole and 8.4 g. of Dye B/silver mole.

Sample Number	Silver Laydown in Layer 17(mg/ft. <sup>2</sup> )	Silver Laydown in Layer 18(mg/ft. <sup>2</sup> )	Shadow Area	Gamma	Highlight Area
1	120	120	0.63		0.98
2	110	135	0.72		0.73
3	85	160	0.98		0.72

The above table illustrates that when the silver laydown is decreased in one side and increased in the other side, the con-

trast of the highlight area decreases while the contrast of the shadow area increases.

Although the invention has been described in considerable with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A direct-positive photographic element comprising a support and at least two layers containing light-sensitive direct-positive compositions which have a substantially light-insensitive 0.1 to 1.5 density layer interposed between said light-sensitive direct-positive layers.

2. A direct-positive photographic element according to claim 1 wherein said light-sensitive layers comprise fogged, direct-positive silver halide grains.

3. A direct-positive photographic element according to claim 1 wherein said light-sensitive layers comprise blue-sensitive-direct-positive silver halide emulsions.

4. A direct-positive element according to claim 1 wherein said light-sensitive layers each comprise fogged direct-positive silver halide emulsions of substantially the same sensitivity.

5. A direct-positive element according to claim 1 wherein at least one of said light-sensitive layers comprises an admixture of at least two portions of silver halide grains.

6. A direct-positive element according to claim 1 wherein at least one of said light-sensitive layers comprises silver halide grains having silver halide cores with a fogged silver halide cover thereon.

7. A direct-positive element according to claim 3 wherein said light-sensitive layers comprise a halogen conductor.

8. A direct-positive element according to claim 1 wherein said light-sensitive layers are at least ten times more sensitive

to light than said light-insensitive interlayer.

9. A direct-positive element according to claim 3 wherein said light-sensitive layers comprise an organic electron acceptor.

10. A direct-positive element according to claim 1 wherein said light-sensitive layers comprise silver halide grains which are fogged by reduction and gold-fogging agents.

11. A direct-positive element according to claim 1 wherein one of said light-sensitive layers comprises a light-absorbing organic dye.

12. A direct-positive element according to claim 1 wherein the furthestmost direct-positive, light-sensitive layer from the support is at least 50 percent thinner than at least one of said light-sensitive underlayers.

13. A direct-positive photographic element comprising (1) a support, (2) at least two layers comprising direct-positive, light-sensitive compositions of substantially the same light sensitivity and (3) means for providing a sensitivity difference in said light-sensitive layers of at least 0.5 log exposure.

14. A direct-positive photographic element according to claim 13 wherein said means is a light-insensitive 0.1 to 1.5 density layer interposed between said light-sensitive layers.

15. A direct-positive photographic element according to claim 13 wherein said means comprises light-absorbing dyes in one of said light-sensitive layers wherein said dyes have an effective absorption in the same region of the spectrum as the sensitivity of the light-sensitive compound of said layer.

16. A direct-positive photographic element according to claim 1 wherein said light-insensitive layer has an effective density of from about 0.3 to about 0.7.

\* \* \* \* \*

35

40

45

50

55

60

65

70

75