

[54] **SILVER HALIDE WITH AN ORTHORHOMBIC LEAD MONOXIDE AND SENSITIZING DYE**

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[*] Notice: The portion of the term of this patent subsequent to Apr. 18, 1989, has been disclaimed.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 195,785, Nov. 4, 1971, abandoned, which is a continuation-in-part of Ser. No. 102,774, Dec. 30, 1970, abandoned.

[52] **U.S. Cl.**..... **96/1.6, 96/1.7, 96/76 R, 96/77, 96/94 R, 96/94 BF, 96/95, 96/99, 96/158, 96/110, 96/114.7, 96/125**

[51] **Int. Cl.**..... **G03g 5/08, G03c 1/28, G03c 1/10**

[58] **Field of Search**..... **96/1.6, 94 BF, 108, 110, 96/125, 76 R, 94 R, 114.7; 252/501**

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[57] ABSTRACT

The present invention relates to photography and, more particularly, to a novel radiation recording photographic element which comprises a photosensitive element which includes, in combination, a particulate dispersion of photosensitive crystals, preferably, photosensitive silver halide crystals adapted to be reduced to silver, upon contact with a silver halide reducing agent, as a function of the crystals' exposure to incident actinic electromagnetic radiation, having associated therewith a sensitizing dye and an orthorhombic lead monoxide semiconductor adapted to donate electrons to the photosensitive crystals as a function of the exposure of the element to incident actinic electromagnetic radiation.

26 Claims, 3 Drawing Figures

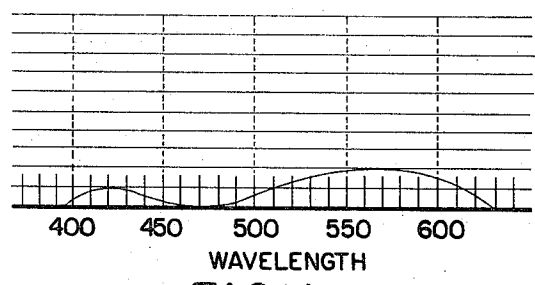


FIG. 1

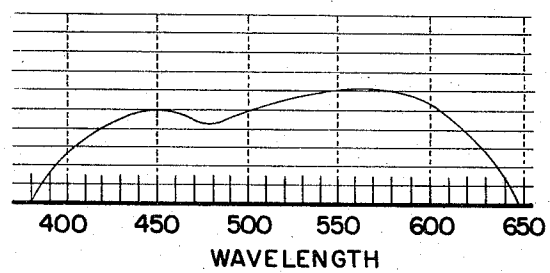


FIG. 2

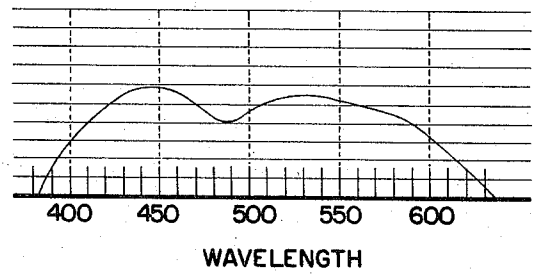


FIG. 3

SILVER HALIDE WITH AN ORTHORHOMBIC LEAD MONOXIDE AND SENSITIZING DYE

CROSS REFERENCE TO OTHER APPLICATIONS

This application is a continuation-in-part of application Ser. No. 195,785 filed Nov. 4, 1971, now abandoned, which is in turn a continuation-in-part of application Ser. No. 102,774 filed Dec. 30, 1970, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to providing new and improved radiation recording photosensitive photographic elements.

2. Description of the Prior Art

In accordance with techniques disclosed in the prior art, photosensitive elements and particularly photosensitive silver halide elements may be provided with increased electromagnetic radiation absorption and photochemical response by specified sensitization procedures.

Among such procedures is found a technique categorized, and denoted, as chemical sensitization, wherein a photosensitive element, and particularly a photosensitive silver halide element, may be treated with compounds such as various sulfur compounds, for example, those set forth in U.S. Pat. Nos. 1,574,944; 1,623,499 and 2,410,689; salts of noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to Group VIII of the Periodic Table of Elements (as set forth in Handbook of Chemistry and Physics, 52nd Edition, 1971-1972, The Chemical Rubber Company, Cleveland, Ohio) and have an atomic weight greater than 100, for example potassium chloroplatinate, sodium chloropalladate, ammonium chlororhodinate, and the like, in amounts below that which produces any substantial fog, as described in U.S. Pat. No. 2,488,060; gold salts, for example, potassium aurothiocyanate, potassium chloraurate, auric trichloride, and the like, as described in U.S. Pat. Nos. 2,597,856 and 2,597,915; reducing agents such as stannous salts, for example, stannous chloride, as described in U.S. Pat. No. 2,487,850, individually or in combination. Such chemical sensitization procedures provide increased response to electromagnetic radiation by the photoresponsive silver halide treated over the frequency range of the inherent, or natural, response characteristics of the crystal.

A second procedure comprises a technique categorized, and denoted, as a spectral, or optical, sensitization procedure, wherein a photosensitive material, and particularly photosensitive silver halide, is provided frequency-selective electromagnetic radiation response characteristics and/or an increase in its inherent, or natural, spectral response characteristics.

In general, such spectral sensitization procedures are accomplished by the adsorption onto one or more surfaces of the photosensitive material of one or more dyes selected from certain classes of dyes including, preferably, cyanine dyes and dyes related to them. For an extensive treatment of cyanine dyes particularly adapted to provide spectral sensitization of, for example, a photosensitive silver halide crystal see Hamer, F. M., *The Cyanine Dyes and Related Compounds*, Interscience Publishers, New York, New York, U.S.A., (1964).

By means of the traditional procedures disclosed in the art as adapted to accomplish spectral sensitization of photosensitive material, and preferably sensitization of photosensitive silver halide, a cyanine dye in the form of polymeric aggregates is adsorbed to the receptive faces, or surfaces, of the photoresponsive material in a statistical monomolecular layer thickness or less. Generally, the cyanine dyes preferably employed for purposes of spectral sensitization comprise an amidinium ion system in which both of the nitrogen atoms are included within separate heterocyclic ring systems, and in which the conjugated chain joining the nitrogen atoms passes through a portion of such heterocyclic ring system. Adsorption is generally believed to be partly accomplished by an unknown type of adsorption between negative crystal surface charges provided, for example, by the excess halide components of the silver halide, and the positive charge of the cyanine chromophore. Adsorption is also favored by the ability to form silver complexes with nuclei containing an amidinium nitrogen atom of a selected cyanine dye's heterocyclic ring system, or systems, for example, with a nuclear sulfur, oxygen, or selenium atom, or a second nuclear nitrogen atom not directly a component of the amidinium ion system.

It has also been understood that the efficiency of the spectral sensitization of a, for example, silver halide crystal increases in accordance with an increase in the adsorption of the selected sensitizing dye, in the form of polymeric aggregates, on the appropriate surfaces, or faces, of the crystal up to the concentration at which increase of sensitivity peaks or plateaus. Specifically, maximum sensitization is understood to occur at a dye concentration level less than or equal to a statistical monomolecular layer of dye coverage on the adsorbing surfaces of the crystal, usually less than a monomolecular coverage of the crystal surface.

Sensitivity conferred by a sensitizing dye thus does not increase proportionately to the concentration of the dye, but rather passes through a maximum as concentration is increased. Attempts to increase the spectral sensitivity of the crystal by increasing the concentration of sensitizing dye adsorbed by its appropriate surfaces beyond the plateau or peak concentration level, provide a progressive decrease in spectral sensitivity as the concentration is so increased; see: Hamer, F. M., *The Cyanine Dyes and Related Compounds*, supra, and Borin, A. V., *Investigation of the Concentration Effect in Optical Sensitization of Photographic Emulsions*, Uspekhi Nauch. Fab. Akad. Nauk. SSSR, Otdel. Ilim. Nauk. 7, 183-190 (1960). In many instances, this resultant decrease in the crystal's spectral sensitivity attains catastrophic proportions when the relative amount of dye necessary to provide a given incremental increase in sensitivity, prior to attainment of the plateau or peak region, is compared with the same amount of dye, in excess of that which provides optimum sensitization.

The energy or charge-carrier absorptive propensity of a photoresponsive element comprising a particulate dispersion of photosensitive material is generally dependent upon the effective, adsorbed presence of sufficient dye to effect maximum absorption of, and transfer of, electromagnetic energy-induced photoreaction stimulus to the photosensitive material. The aforementioned "monomolecular layer" adsorption of the dye to the appropriate surfaces of the photosensitive material

fails, by a relatively large degree, to provide complete absorption of incident radiation. In fact, in conventional optically sensitized, photographic, photoresponsive elements, such as panchromatic photographic emulsions, coated on a suitable supporting member, comprising a relatively thin layer, for example, on the order of about 7 microns in thickness, and including a dispersion of photoresponsive silver halide in a gelatin matrix, for example, in a concentration of about 100 mgs. of silver per square foot, the photoresponsive element only absorbs roughly in the order of less than one-third of the available incident light, over the radiation frequency range desired for photographic employment of the element, with the concomitant failure of such elements to even approximate their potential, or theoretical, efficiency. The maximum absorbed radiation attributable to a given monomolecular dye layer adsorbed on a photosensitive crystal is about seven percent of the total incident radiation; W. West and V. I. Saunders, *Wissenschaftliche Photographie*, W. Eichler, H. Friese and O. Helwich, eds., Verlag Dr. O. Helwich, Darmstadt, 1958, P. 48. The net response of the system thus cannot be improved by simply adding more of the same sensitizing dye, but must be achieved by development of more efficient and effective sensitizing dye systems.

Photographic action may be considered to be the result observed upon transfer of an electron or energy stimulus to a photosensitive material such as a photosensitive silver halide crystal. Thus, in practice it may be measured by an evaluation of the degree of photochemical change produced in a given photosensitive material by such a stimulus, which renders individual grains developable thus producing the requisite image formation. The above-indicated stimulus which alters the characteristics of the photosensitive material is transferred to the photosensitive material either directly from incident electromagnetic radiation or from a dye adsorbed or associated with said photosensitive material. Such photographic action is a function of both the quanta of stimulus absorbed and the relative quantum efficiency of the adsorbed quanta; the quantum efficiency being considered to be a measure of the quanta which initiate photochemical changes relative to the total quanta absorbed.

In an attempt to avoid or minimize the foregoing problems, the art has attempted to adopt, in applicable instances, a technique denoted as supersensitization. Specifically, the art employs a technique which comprises absorbing to a photosensitive crystal surface a monomolecular layer of a plurality of synergistic components, at least one of which comprises a cyanine dye and generally, but not necessarily, all of which comprise a selected plurality of different cyanine dyes in an attempt to provide an increase in photon excitation quantum efficiency; however, the techniques development to date has frequently merely acted to decrease the inevitable desensitizing propensities of the cyanine dye optical sensitizing agents traditionally employed in the art.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved radiation recording photographic element which comprises a photosensitive element which includes, in combination, a particulate dispersion of photosensitive crystals, preferably, silver halide crystals

adapted to be reduced to silver, upon contact with a silver halide reducing agent, as a function of the exposure of the crystals to incident actinic radiation, having associated therewith a sensitizing dye and an orthorhombic lead monoxide semiconductor adapted to amplify the photosensitivity of the crystals to incident actinic radiation. The term "PbO" as used herein will refer to orthorhombic lead monoxide.

In a specifically preferred embodiment of the present invention, the sensitizing dye and orthorhombic lead monoxide semiconductor are associated with photosensitive silver halide crystals in electron donating relationship and are specifically adapted to donate electrons to the silver halide crystals, as a function of exposure to incident electromagnetic radiation, to thereby selectively induce increased photoresponse to the crystals within and/or without the electromagnetic radiation spectrum range to which the crystals are inherently responsive.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of the action spectra, as determined on a wedge spectrograph, of a silver iodochlorobromide emulsion sensitized with a sensitizing dye in accordance with the prior art;

FIG. 2 is a graphical representation of the photoreponse action spectra, as determined on a wedge spectrograph, of a silver iodochlorobromide emulsion sensitized with a sensitizing dye to which has been added a particulate dispersion of a semiconductor in accordance with the present invention; and

FIG. 3 is a graphical representation of the photoreponse action spectra, as determined on a wedge spectrograph, of a silver iodochlorobromide emulsion to which has been added a premixed combination of a sensitizing dye and a particulate dispersion of a semiconductor in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Commensurate with the present invention, enhancement of the photographic action of a photoresponsive material may be achieved by the amplification of electron transfer to said photoresponsive material from an associated electron source which comprises a sensitizing dye and an orthorhombic lead monoxide semiconductor adapted to provide electron flow in response to incident electromagnetic radiation.

In general, the absorption of photon excitation derived activating energy, e.g., a photon, by a photoresponsive crystalline material results in the excitation of an electron from a lower energy state to a higher energy state in the structure of the crystal. An excited electronic state is thereby provided to the photoresponsive material resulting in the production of free electrons and sites, where the electrons were situated prior to the impingement of the activating radiation, which act as positively charged particles, i.e., positive "holes."

Silver halide, which itself is a semiconductor, contacted with an activating photon generates an electron moving from the valence band to the conduction band where, in its excited state, it is available to move freely, become trapped and contacted by an available interstitial silver ion, i.e., interstitial Ag^+ ion, thereby forming a latent image adapted to be converted to a visible photographic signal.

The thus-formed latent image in the silver halide photoresponsive material is adapted to be developed, or reduced, by conventional procedures of the art to provide a visible species by contact with reagents which will react differentially between the exposed, i.e., pos-

sessing latent image, and unexposed photoresponsive material.

This phenomenon of excitation of photoresponsive material is treated in further detail in the extensive literature of the photographic art, for example, see Mees' *Theory of Photographic Process*, 3rd Edition, MacMillan Company, 1967, Chapter 1, etc.

As is also known in the prior art, response of photosensitive materials may be extended, that is, the wavelength range to which a selected photosensitive material is responsive may be extended, or the photographic response of photosensitive material within the inherent range of its absorption increased, by the addition of one or more sensitizing dye materials. Such sensitizing dye materials function to provide the photoresponsive material with additional electrons in response to impinging radiation of wavelengths to which the sensitizing material and/or photoresponsive material is sensitive. Long wavelength range extension of the photographic action of photoresponsive materials thus has been conventionally achieved in the art as described above by employing a sensitizing dye material which can be specifically characterized as a material adapted to provide electrons to a photoresponsive material in response to activating energy incident on the system.

By the employment of a sensitizing dye for a photosensitive material, which dye is also an energy transmitting material, and an inorganic semiconductor adapted to donate electrons to the photosensitive material as a function of incident electromagnetic radiation, however, unexpected enhancement of the photographic action of a photoresponsive material can be achieved. The amplification effect thus obtained is not merely of the additive type nor an upgrading of the function of the sensitizing dye, but rather results in advantageous and unexpected properties to a degree not obtainable with conventional systems and methods known to the art.

A variety of photoresponsive materials are suitable for use in the present invention. The most commonly employed photoresponsive materials are photosensitive metallic halides, such as the silver halides, i.e., silver chloride, silver bromide, silver iodide, and mixed halides such as silver iodobromide and silver iodochlorobromide and the like. Other metallic halides include lead halide and thallium halides. As detailed hereinafter, inorganic photoconductive materials such as zinc oxide and titanium dioxide and organic photoconductive materials such as anthracene and polyvinylcarbazole may also be employed in the practice of the present invention as the photoresponsive component.

The term "photoresponsive" as employed throughout the present specification is thus intended to refer to a material adapted to receive activating energy of selected wavelengths incident thereon which, as a result of the incident radiation, is adapted to undergo modification to provide a photographic signal, either not obtainable in unexposed material or not obtainable at an effective differential rate.

The sensitizing dyes employed in the present invention provide the aforementioned extension to the

photoresponsivity of the selected photoresponsive material, i.e., provide additional electrons to the photoresponsive material as a function of activating energy impinging on the photoresponsive material and/or on the sensitizing dye. The sensitizing dye itself may also possess the ability to function as an energy transfer bridge, i.e., a conductive material, to not only provide electrons originating therein to the photoresponsive material, but also to accept and transmit electrons from the inorganic semiconductor, which latter element may act to provide electrons in response to the radiation incident on the photoresponsive material, the semiconductor and/or the sensitizing dye.

The sensitizing dyes to be employed in the practice of the present invention are conventional and well-known art materials definitely described and detailed in *The Cyanine Dyes and Related Compounds*, supra, and the extensive multiplicity of both U.S. and foreign patents relating to photographic spectral sensitization employing optical sensitizing dyes.

The orthorhombic lead monoxide semiconductor to be employed is adapted to provide electrons to the remaining components of the trielement system in response to activating energy impinging on said system. Thus, assuming photons are adsorbed directly or indirectly by the photoresponsive component of the system within the scope of the present invention, the electrons in the photoresponsive material would be made available as free electrons for latent image formation. The sensitizing dye provides enhanced, and/or spectral, sensitization of the photoresponsive material by implementing an electron flow into said photoresponsive material in response and as a function of photoexposure. By thus creating an electron deficiency in the sensitizing dye and/or photoresponsive component, an electron output is also implemented in the inorganic semiconductor material. While it is understood that the deficiency of the electrons in the sensitizing dye, i.e., positive "holes," resultant from transfer of electrons to the photoresponsive material, would attract electrons, and as a result of a subsequent build-up of electrons in said sensitizing dye, cascade still more electrons to the photoresponsive material by reason of the limited electron capture cross section of the dye as associated with the material, in certain instances the electron flow may be in whole or in part directly from the inorganic semiconductor material to the photoresponsive material.

The foregoing description of the mechanism of the photographic system of the present invention has been described with respect to activating energy impinging on the photoresponsive material. It should be understood that similar electron transfer will result if the activating energy impinges on the sensitizing dye solely, i.e., the activating energy is of a wavelength absorbed by the sensitizing dye alone or which may be absorbed by both the photoresponsive material and the sensitizing dye.

It is unexpected that orthorhombic lead monoxide would function to provide the increased photoresponse described above since tetragonal lead monoxide does not provide the same result. Some other metal oxides also fail to show the effects provided by orthorhombic lead monoxide.

It has been found that the methods of preparing the photoresponsive elements are not critical in the present invention. Binders for the photoresponsive material or the lack thereof are also not critical and the present in-

vention is directed to photoresponsive materials both retained in binder materials, again referring to the photosensitive silver halide in gelatin, for example, or an entirely binderless material, for example, vacuum deposited materials.

By means of the present invention a photoresponsive system is thus provided which is capable of photocurrent amplification leading to latent image formation without the application of an external field.

In conventional spectral sensitization of, for example, silver halides by adsorbed organic dyes, it is found that the photographic quantum efficiency in the spectrally sensitized region is generally lower than the quantum efficiency in the inherent region in the absence of the sensitizer and that the dye sensitization, accordingly, may be interpreted in terms of electronic p-n junction effects. These systems or devices are or function as solid state diodes. However, such solid state diodes are not amplifiers and no amplification effect has been noted to date. The addition of the third junction to such a diode, however, can convert such a device into a transistor or transistor-like system with its resultant potential amplification. Thus, the novel systems of the present invention employing an orthorhombic lead monoxide semiconductor as the material to provide the second junction may be directly analogized to a transistor. In point of fact, a gain in photographic action greater than a factor of eight has been achieved without the application of an external electronic field.

Specifically, trielement systems of the type described were tested employing silver chlorobromide gelatin emulsions as well as binderless systems, in combination with panchromatic, blue, green and red sensitizing dyes, respectively, and an orthorhombic lead monoxide (PbO) semiconductor. In such a system, the dye is considered to serve as the base of the transistor.

It is understood that the addition of a p-type sensitizing dye to an n-type photosensitive crystalline material sets up a space charge at the interface due to equalization of the Fermi levels in the two phases. The crystalline material becomes positively charged and the sensitizing dye negative in the instance where the Fermi level of the material exceeds that of the dye. The further addition of the n-type semiconductor then requires a second readjustment of the Fermi levels to provide n-p-n junction.

Exposure in the spectral region where only the sensitizing dye absorbs light, i.e., outside of the inherent sensitivity range of the photosensitive crystalline material selected, results in migration of electrons into the photosensitive crystals comprising the photoresponsive material in a manner conventional to the art in the absence of the third component of the system. The electron donating PbO, however, senses an increase in the number of positive holes in the sensitizing dye as a result of said migration and/or in the photosensitive crystal when photoexcited within the inherent region and responds by liberation of electrons; thus, amplifying the flow of electrons into the crystal by the additive effect of secondary electrons emitted by the PbO semiconductor phase.

In the above-described systems of the present invention, photographic efficiency in the spectral region where only the dye absorbs light has been found in many instances to be approximately eight times higher when a semiconductor is employed as compared to the two component, or diode, system and the spectral ab-

sorption range of the systems are generally unaltered by the presence of semiconductor. Estimation of the photographic efficiency in the dye absorption region when a PbO semiconductor is present as compared to the inherent region in the absence of any sensitizer, indicates also that the efficiencies may be roughly equivalent and in certain instances higher with respect to the dye absorption region. The amplification also appears to occur irrespective of the presence of the semiconductor possessing a longer wavelength absorptive edge than the absorption edge of a sensitizing dye selected.

Specifically with reference to the electron transfer mechanism, sensitization of the photographic process is understood to occur by the passage of electrons to the conduction band of the silver halide crystals from the sensitizing material and/or semiconductor material, optically excited as a result of incident actinic radiation whether from the PbO semiconductor to the sensitizing material and in turn as a cascade to the silver halide crystals and/or directly to the silver halide crystals upon optical excitation of the sensitizing material; and/or from the semiconductor to the silver halide crystals upon optical excitation of the crystals and/or the semiconductor within the spectral region of their respective photosensitivity. More specifically, when a silver halide crystal, which may be considered an n-type semiconductor, having a band gap energy higher than that of a selected sensitizing dye is brought into contact with the sensitizing dye, which may be considered a p-type semiconductor having a lower Fermi level, a lesser band gap energy level and a higher conduction band level than that of the silver halide crystal, and the PbO semiconductor also possessing a higher Fermi level, larger band gap energy level and higher conduction band level, i.e., a higher first excited state, than the silver halide crystal preferably also possessing a higher Fermi level, larger band gap energy level and lower conduction band level than the sensitizing dye, certain changes are believed immediately to take place prior to photoexposure. Specifically, there is believed to be a flow of electrons from the n-type silver halide to the p-type sensitizing dye and, in turn, from the semiconductor to the p-type dye, resulting in an equalization of the Fermi levels of the respective materials. Consequently, in accordance with well-known semiconductor theory (see, for example, Nassbaum, A., *Semiconductor Device Physics*, Prentice Hall, N.J. 1962, at page 93, and Bube, R. H., *Photoconductivity of Solids*, John Wiley and Sons, New York, 1960, at page 78), as a result of the increased concentration of electrons in the p-type sensitizing dye and corresponding increased concentration of positive holes in the n-type silver bromide, a space charge is developed in the region of the interface which extends into the respective bulk phases for distances of the order of a micron. (With small particulate materials such as silver halide crystals, this space charge may extend throughout a significant portion of the system). The polarity is such as to leave the n-type silver halide positively charged, the p-type sensitizing dye negatively charged and the semiconductor positively charged.

Upon exposure to light, absorption of light by the p-type sensitizing dye, for example, beyond the region of intrinsic absorption of the silver halide raises electrons from the valence band into the conduction band of the sensitizing dye and/or semiconductor. Owing to the space charge which was established prior to exposure,

electrons are now able to flow across the interface from the sensitizing dye and/or semiconductor to the silver halide, at which point they become available for latent image formation. Practically speaking, this results in new peaks in the action spectrum of the sensitized silver halide as compared with that of the unsensitized material.

The preferred silver halide dispersions employed for the fabrication of preferred photographic film units comprising sensitized photoresponsive silver halide crystals, as specifically detailed immediately above, may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or, alternatively, employing any of the various flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,614,929; 2,728,662; and like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and/or such other polymeric materials as may be desired and various adjuncts, for example, the previously detailed chemical sensitizing agents and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography Its Materials and Processes*, 6th Ed., 1962.

Specifically, a gelatino silver iodobromide emulsion prepared as detailed above and comprising a gelatin/silver ratio of about 1:1 and about four mole percent iodide concentration may be chemically sensitized with gold and sulfur as, for example, by the addition, at about 56°C., pH 5 and pAg 9, of an optimally sensitizing amount of a solution comprising 0.1 gram of ammonium thiocyanate in 9.9 cc. of water and 1.2 cc. of a solution containing 0.097 gram of gold chloride in 9.9 cc. of water, and a 0.02 percent aqueous sodium thiosulfate solution.

Optical sensitization of the dispersion's silver halide crystals may then be accomplished by contact of the emulsion composition with an effective concentration of the selected cyanine optical sensitizing dye or dyes, each of which dyes has preferably been dissolved in an appropriate dispersing solvent such as methanol, ethanol, pyridine, acetone, water, and the like; all according to the traditional procedures set forth in the art such as, for example, the U.S. and foreign patents referred to herein. In general, the concentration of sensitizing dye or dyes may be varied empirically in accordance with the characteristics of the particular photoresponsive material such as the silver halide selected and the sensitizing effects desired which in the instance of preferred silver iodobromide dispersions will ordinarily fall within the range of about 0.05 to 5 grams per 100 grams of silver halide measured as silver.

Specifically, the formulation may be optically sensitized in accordance with the present invention by the addition of a sensitizing concentration of one or more of the cyanine optical sensitizing dyes detailed herein

as, for example, 1, 2 and 4 mgs. per gram of silver of the cyanine dye of Formula 1 dissolved in methanol.

Alternatively, an emulsion coating can be prepared and coated on a suitable support whereupon the coating may be sequentially immersed in respective solutions of selected cyanine dyes.

The orthorhombic lead monoxide semiconductor may be incorporated in the formulation contemporaneous with or subsequent to optical sensitization.

It is preferred, however, that for most systems within the scope of the present invention, the dye or the dye-semiconductor mix be added to the silver halide prior to the semiconductor alone.

Specifically, the semiconductor may be provided to the formulation by suspension in particulate form in a liquid medium in which it is insoluble and which is non-deleterious to photographic emulsions, such as water, methanol or other lower molecular weight alcohol, or a mixture of water and alcohol; the suspension so formed is then added to and mixed throughout the above-described formulation.

Alternatively, the silver halide may be precipitated in the presence of the PbO semiconductor in such a way that a core-shell configuration is obtained, with either material, i.e., the silver halide crystal or a lead oxide particle, comprising either the core or the shell.

With respect to semiconductor/silver halide ratio, widely varying ratios have been observed to be effective. In particular, silver halides have been effectively sensitized according to the present inventive concept, by utilizing molar ratios from one silver halide:one semiconductor to one silver halide:0.01 semiconductor, although higher or lower ratios may be suitable, depending upon emulsion and sensitization characteristics desired.

The particle size of the semiconductor particles has been found not to be critical, except that it will be obvious to those familiar with semiconductor theory that the particle size and configuration must be such as to provide for adequate interfacial contact between the silver halide crystals, sensitizing dye and semiconductor particles. In practice, sonified suspensions of semiconductor have been found to give particularly good results, since the submicroscopic particles may then in part form a layer on the silver halide crystal. However, it will be appreciated from the foregoing discussion of theoretical considerations that the sensitizing activity of the semiconductor is not dependent upon the formation of an actual semiconductor layer as such; rather, electron transfer can take place readily provided there is at least minimum effective electronic contact between respective reactants. Insofar as silver halide sensitization and amplification is concerned, there is no theoretical maximum particle size for the semiconductor. However, the particles should be of sufficiently small size, as well as concentration, so as not to interfere with the photographic characteristics of the silver halide emulsion, as by reflecting and/or scattering incident actinic radiation to any significant extent. Thus, for example, for conventional silver halide emulsion layers having a thickness of about 0.6 to 20 microns wherein the silver halide grains present have an average particle size distribution in the order of 0.1 to 10 microns, it is preferred that the semiconductor particles be present at an average particle size distribution of 0.1 to 10 microns or less. Obviously, the smaller the semiconductor particle size, the less the quantity of semi-

conductor on an absolute weight basis required to amplify the sensitivity of a given quantity of a photosensitive silver halide crystalline material. It will be appreciated that absolute numbers as applied to a specific semiconductor particle size and ratio to a silver halide are only meaningful with respect to a single specified silver halide system and that one of ordinary skill in the art possessing the present invention would readily be able to determine empirically the specific parameters which must be utilized to give optimum sensitizing results in the practice of the invention.

It will be recognized that semiconductor particles for use within the scope of the present invention may be readily prepared by any of the conventional techniques, for example, ball mill, sand grinding, ultrasonic, and the like, for the production of particulate solid materials. In general, a wet paste comprising solid semiconductor particles, and optionally, one or more dispersing agents, surfactants, antifoamers, antioxidants, or the like, and water may be processed according to the identified techniques to provide particles of the size desired and the output of the process selected, where desired, may be appropriately filtered to effect removal of any particles which may be present exceeding that of a diameter within the particle size range desired.

Conventional sand grinding techniques adapted to mill solid particles such as to provide the requisite particle size distribution generally comprise agitating an aqueous semiconductor slurry with a sand, which, for example, may possess a size range of 20 to 40 mesh, until the desired particle size distribution is obtained and then separating the semiconductor from contact with the abrasive sand. Commercial mills, of various capacities, adapted to perform sand grinding, may be procured from the Chicago Boiler Company, Chicago, Ill., U.S.A.

For the preparation of semiconductor material possessing the desired particle size distribution by ultrasonic techniques, an aqueous semiconductor slurry may be treated employing commercial sonifiers such as those procured from Bronson Instruments, Incorporated, Stamford, Conn., U.S.A.

Subsequent to sensitization, any further desired additives, such as coating aids and the like, may be incorporated in the emulsion and the mixture coated and processed according to the conventional procedures known in the photographic emulsion manufacturing art.

The sensitized formulation may then be coated on an appropriate support as, for example, cellulose triacetate film base and the film units thus prepared exposed in a conventional wedge spectrograph to detail wavelength specific sensitivity of the formulation to incident electromagnetic radiation.

Upon processing with a photographic developing composition as, for example, a conventional processing composition of the type commercially distributed by Eastman Kodak Company, Rochester, N.Y., U.S.A., under the trade name of "Dektol Developer" and comprising an aqueous alkaline solution of monomethylpara-amino phenol sulfate and hydroquinone, and a conventional acid stop bath, the resultant spectrograms will detail the sensitivity characteristics of the optically sensitized formulation which may be directly compared with a nonoptically sensitized film unit of film units optically sensitized with selected prior art dyes.

As previously detailed, the photoresponsive crystals of the present invention may be employed as the photosensitive component of a photographic emulsion by incorporated within a suitable binder and the coating and processing of the thus prepared emulsion according to conventional procedures known in the photographic manufacturing art.

The photoresponsive crystal material of the photographic emulsion will, as previously described, preferably comprise a crystal of a silver compound, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver iodobromide or silver iodochlorobromide or varying halide ratios and varying silver concentrations. The formulated photographic emulsions may be used for the preparation of orthochromatic, panchromatic and infrared sensitive photographic films.

The fabricated emulsion may be coated onto various types of rigid or flexible supports, for example, glass, paper, metal, polymeric films of both the synthetic types and those derived from naturally occurring products, etc. Especially suitable materials include paper; aluminum; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycol terephthalic acid; polymeric cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-butyrates, or acetate-propionate; polycarbonates, polystyrenes, etc.

The emulsions may include the various adjuncts, or addenda, according to the techniques disclosed in the art, such as speed increasing compounds of the quaternary ammonium type, as described in U.S. Pat. Nos. 2,271,623; 2,288,226; and 2,334,864; or of the polyethyleneglycol type, as described in U.S. Pat. No. 2,708,162; or of the preceding combination, as described in U.S. Pat. No. 2,886,437; or the thiopolymers, as described in U.S. Pat. Nos. 3,046,129 and 3,046,134.

The emulsions may also be stabilized with the salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, as described in U.S. Pat. Nos. 2,566,245 and 2,566,263; the mercury compounds of U.S. Pat. Nos. 2,728,663, 2,728,664 and 2,728,665; triazoles of U.S. Pat. No. 2,444,608; the azaindines of U.S. Pat. Nos. 2,444,605; 2,444,606; 2,444,607; 2,444,609; 2,450,297; 2,713,541; 2,716,062; 2,735,769; 2,743,181; 2,756,147; 2,772,164; and those disclosed by Burr in "Wiss. Phot.", Vol. 47, 1952, pages 2-28; the disulfides of Belgian Pat. No. 569,317; the benzothiazolium compounds of U.S. Pat. Nos. 2,131,038 and 2,694,716; the zinc and cadmium salts of U.S. Pat. No. 2,839,405; and the mercapto compounds of U.S. Pat. No. 2,819,965.

Hardening agents such as inorganic agents providing polyvalent metallic atoms, specifically polyvalent aluminum or chromium ions, for example, potash alum $[K_2Al_2(SO_4)_4 \cdot 24H_2O]$ and chrome alum $[K_2Cr_2(SO_4)_4 \cdot 24H_2O]$ and inorganic agents of the aldehyde type, such as formaldehyde, glyoxal, mucchloric acid, etc.; the detone type such as diacetyl; the quinone type; and the specific agents described in U.S. Pat. Nos. 2,080,019; 2,725,294; 2,725,295; 2,725,305;

2,726,162; 2,732,316; 2,950,197; and 2,870,013, may be incorporated in the emulsion.

The emulsion may also contain one or more coating aids such as saponin; a polyethyleneglycol of U.S. Pat. No. 2,831,766; a polyethyleneglycol ether of U.S. Pat. No. 2,719,087; a taurine of U.S. Pat. No. 2,739,891; a maleopimarate of U.S. Pat. No. 2,823,123; an amino acid of U.S. Pat. No. 3,038,804; a sulfosuccinamate of U.S. Pat. No. 2,992,108; or a polyether of U.S. Pat. No. 2,600,831; or a gelatin plasticizer such as glycerin; a dihydroxyalkane of U.S. Pat. No. 2,960,404; a bisglycolic acid ester of U.S. Pat. No. 2,904,434; a succinate of U.S. Pat. No. 2,940,854; or a polymeric hydrosol of U.S. Pat. No. 2,852,386.

As the binder for photosensitive crystals, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin, casein; or zein; or resins such as cellulose derivatives and vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents.

The photographic emulsions may be employed in black-and-white or color photographic systems, of both the additive and subtractive types, for example, those described in *Photography, Its Materials and Processes*, supra.

The fabricated emulsions may also be employed in silver diffusion transfer processes of the types set forth in U.S. Patents Nos. 2,352,014; 2,500,421; 2,543,181; 2,563,342; 2,565,376; 2,584,029; 2,584,030; 2,603,565; 2,616,807; 2,635,048; 2,644,756; 2,647,055; 2,662,822; 2,698,236; 2,698,237; 2,698,238; 2,698,245; 2,702,244; 2,704,721; 2,740,715; 2,759,825; 2,774,667; 2,823,122; 2,923,623; 2,938,792; 2,962,377; 2,984,565; 3,003,875; 3,043,690; 3,087,815; 3,087,816; 3,091,530; 3,108,001 and 3,113,866; in additive color diffusion transfer processes of the types disclosed in U.S. Pat. Nos. 2,614,926; 2,726,154; 2,944,894; 2,992,103 and 3,087,815; and in subtractive color diffusion transfer processes of the types disclosed in U.S. Pat. Nos. 2,559,643; 2,600,996; 2,614,925; 2,647,049; 2,661,293; 2,698,244; 2,698,798; 2,774,668; 2,802,735; 2,855,299; 2,892,710; 2,909,430; 2,968,554; 2,983,605; 2,983,606; 2,992,104; 2,992,105; 2,992,106; 2,997,390; 3,003,872; 3,015,501; 3,019,104; 3,019,124; 3,022,166; 3,022,167; 3,039,869; 3,043,689; 3,043,692; 3,044,873; 3,047,386; 3,065,074; 3,069,262; 3,069,264; 3,076,808; 3,076,820; 3,077,400; 3,077,402; 3,148,062; 3,227,550; 3,227,551; 3,227,554; 3,243,294; 3,364,022; 3,443,939; 3,443,940; 3,443,941; 3,443,943; 3,415,644; 3,415,645; 3,415,646; 3,473,925; 3,573,042; 3,573,043; 3,573,044; 3,576,625 and 3,576,626; etc.

The photoresponsive crystals of the present invention may also be employed as the photosensitive component of information recording elements which employ the distribution of a dispersion of relatively discrete photoresponsive crystal, substantially free from interstitial binding agents, on a supporting member such as those previously designated, to provide image recording elements, for example, as described in U.S. Pat. Nos. 2,945,771; 3,142,566; 3,142,567; Newman, *Comment on Non-Gelatin Film*, B.J.O.P., 534, Sept. 15, 1961; and Belgian Pat. Nos. 642,557 and 642,558.

As taught in the art, the concentration of silver halide crystals forming a photographic emulsion and the rela-

tive structural parameters of the emulsion layer, for example, the relative thickness, and the like, may be varied extensively and drastically, depending upon the specific photographic system desired and the ultimate employment of the selective photographic system.

In conventional photographic processes, for the formation of silver images, a latent image is provided by selective exposure of a photosensitive photographic emulsion, generally containing the aforementioned photoresponsive silver halide crystals or the like. The thus-produced latent image is developed, to provide a visible silver image, by a suitable contact with any of the photographic developing solutions set forth in the art. For the purpose of enhancing the resultant visible image's stability, the image may be suitably fixed, according to the procedures also well known to those skilled in the art. The resultant image-containing element may be then directly employed or, optionally, may be employed, where applicable, as a negative image, for example, to provide a reversed or positive image by conventional contact or projection printing processes employing suitable photosensitive printing papers.

In the conventional photographic subtractive color processes which find extensive commercial utilization, color coupling techniques are generally employed to provide the requisite number of registered color images necessary for monochromatic and multichromatic reproduction. According to these techniques, one or more selectively photoresponsive, generally gelatinous, silver halide strata are selectively exposed to provide latent image record formation corresponding to the chromaticity of the selected subject matter. The resultant latent images are suitably developed by selective intimate contact between one or more color developing agents and one or more color formers or couplers to provide the requisite negative color images. Alternatively, the latent images are developed to provide visible silver images; the resultant visible images removed; the remaining residual silver halide exposed, and the second-formed exposure records developed by selective contact between one or more color developing agents and one or more color formers or couplers, in the presence of exposed silver halide to provide the desired colored positive image.

In diffusion transfer processes, for the formation of positive silver images, a latent image contained in an exposed, photosensitive, generally gelatinous, silver halide emulsion is developed and, substantially contemporaneous with development, a soluble silver complex is obtained by reaction of a silver halide solvent with the unexposed and undeveloped silver halide of the emulsion. The resultant soluble silver complex is, at least in part, transported in the direction of a suitable print-receiving element, and the silver of the complex precipitated in such element to provide the requisite positive image definition.

Additive color reproduction may be produced by exposing a photosensitive silver halide emulsion through an additive color screen having filter media or screen elements, each of an individual additive color such as red, blue or green, and by viewing the resultant image, subsequent to development, through the same or a similar screen element. Alternatively, the photosensitive element may be employed to provide a silver transfer image analogous to the preceding description of diffusion transfer processing and the resultant transfer

image may be viewed through the same, or a similar, additive color screen which is suitably registered with the silver transfer image carried by the print-receiving image.

Subtractive color reproduction may be provided by diffusion transfer techniques wherein one or more photoresponsive spectrally selective silver halide elements, having an appropriate subtractive color-providing material associated therewith, are selectively exposed to provide the requisite latent image record formations corresponding to the chromaticity of the selected subject matter and wherein the distribution of color-providing materials, by diffusion, to a suitable image-receiving element, is controlled, imagewise, as a function of the respective latent image record formations. Particularly preferred color-providing materials comprise dye image-forming materials adapted to provide an imagewise distribution of diffusible dye as a function of the point-to-point degree of photosensitive element photoexposure and, in particular, dye image-forming materials which comprise a dye which is a silver halide developing or reducing agent adapted to provide an imagewise distribution of diffusible dye in terms of the unexposed areas of the photosensitive element. An extensive multiplicity of such preferred dyes is disclosed in aforementioned U.S. Pat. No. 2,983,606, and including specifically the copending U.S. applications cross-referenced at column 27 thereof.

In addition to the selectively sensitized photoresponsive components generally employed to provide multicolor reproduction by means of the principles of subtractive color photography, the novel photoresponsive materials of the present invention are also particularly suitable for employment to provide a panchromatically sensitized silver halide emulsion specifically adapted for employment for color reproduction by means of aforementioned additive multicolor diffusion transfer process techniques. Specifically, a panchromatic silver halide emulsion provided in accordance with the present invention is exposed through a conventional additive color screen having a plurality of filter media or screen element sets, each of an individual additive color, such as red, green or blue, and by viewing the resultant diffusion transfer process photographic image subsequent to development of such image, through the same or a substantially identical screen element suitably registered.

Although, as disclosed in aforementioned U.S. Pat. No. 2,614,926, the positive silver transfer image formation may be provided by an additive multicolor diffusion transfer reversal process which includes exposure of a silver halide emulsion layer through an additive color screen and separation of the emulsion layer, from contact with the remainder of the film unit, subsequent to processing, while retaining filter media and reception layer in fixed relationship, an alternative process will comprise that disclosed in aforementioned U.S. Pat. Nos. 2,726,154 and 2,944,894, which are directed to a diffusion transfer reversal process which specifically includes exposure of an integral multilayer film assemblage through a screen possessing a plurality of minute optical elements and carrying photosensitive and image-receiving layers. As disclosed in the cited patents, transfer processing of the exposed film may be accomplished by permeation of the exposed integral film unit with a liquid processing composition and the image-receiving layer retained in permanent fixed rela-

tionship to the screen during, and subsequent to, formation of the requisite transfer image, with the operator's option of separating the photosensitive layer from the remainder of the film unit subsequent to transfer image formation.

Improved integral silver diffusion transfer film assemblages essentially comprising photoresponsive material directly providing positive image formation and possessing the sensitivity to incident electromagnetic radiation and acuity of image formation necessary to effectively provide photographic image reproduction, both black-and-white and assemblages including optical screen elements to provide color photographic image reproduction, are disclosed and claimed in the copending applications Ser. Nos. 736,796; 889,656; 889,657; 889,660; and 889,636, filed June 13, 1967; Dec. 31, 1969; Dec. 31, 1969; Dec. 31, 1969; and Dec. 31, 1969, respectively, which are directed in general to film unit assemblages and comprise a permanently fixed laminate which includes a support carrying on one surface photosensitive silver halide crystals and silver precipitating nuclei.

The photoresponsive crystals of the present invention may also be employed as the photoconductive component of electrophotographic materials, for example, inorganic photoconductive crystals such as zinc oxide, selenium, cadmium sulfide, cadmium telluride, indium oxide, antimony trisulfide, and the like, and organic photoconductive crystals such as anthracene, sulfur, benzidine, the aromatic furanes of U.S. Pat. No. 3,140,946, and the like, as described in U.S. Pat. No. 2,987,395; 3,047,384; 3,052,540; 3,069,365; 3,110,591; 3,121,008; 3,125,447; and 3,128,179.

In preparing photoconductive layers, it is the usual practice to suspend the photoconductive crystal in a suitable solvent in the presence of an electrically insulating binder and then to dissolve the optical sensitizing dye in this composition prior to coating on a conducting support. Where the layers are thus prepared, the optical sensitizing components are added to the coating composition, prior to coating, in the manner of the instant invention as described hereinbefore.

Alternatively, an unsensitized photoconductive layer can be prepared and the coating then sensitized according to the previously described alternate procedure.

Preferred binders for use in preparing the photoconductive layers comprise polymers having fairly high dielectric strength and which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; silicone resins; styrene-alkyd resins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidene chloride); vinylidene chloride, acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate, vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene; isobutylene polymers; polyesters, such as poly(ethylene-alkaryloxy-alkylene terephthalate); phenol-formaldehyde resins; ketone resins; polyamides; polycarbonates, etc. Methods of making resins of this type have been described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Pat. Nos. 2,361,019 and 2,258,423. Other types of binders which can be used in

the photoconductive layers include such materials as paraffin, mineral waxes, and the like.

Solvents of choice for preparing the last-mentioned coating compositions can include a number of solvents such as benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc.

The photoconductive layers can then be coated on a conducting support in any well-known manner such as the conventional doctor-blade coating, swirling, dip-coating, and the like, techniques. Although photoconductive layers in some cases do not require a binder, it is usually beneficial to include some binder in a coating composition of this type, for example, as little as 1 weight percent.

In preparing the coating composition, useful results will be obtained where the photoconductor substance is present in an amount equal to at least about 1 weight percent of the coating composition. The upper limit in the amount of photoconductor substance present is not critical. As indicated previously, the polymeric materials in many cases do not require a binder in order to obtain a self-supporting coating on the support. In those cases where a binder is employed, it is normally desired that the photoconductive substance be present in an amount from about 1 weight percent of the coating composition to about 99 weight percent of the coating composition. A preferred weight range for the photoconductor substance in the coating composition is from 10 weight percent to about 60 weight percent.

Coating thicknesses of the photoconductive composition on a support can vary widely. Normally a wet coating in the range from about 0.001 inch to about 0.01 inch is useful. A preferred range of wet coating thickness may be found to be in the range from about 0.002 inch to about 0.006 inch.

Suitable supporting materials for the photoconductive layers of the present invention can include any of the electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foils, such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass, and galvanized plates, regenerated cellulose and cellulose derivatives; certain polyesters and especially those having a thin electroconductive layer (e.g., cuprous iodide) coated thereon; and the like.

The photoconductive elements can be employed in any of the well-known electrophotographic processes which require photoconductive layers. One such process is the xerographic process. In a process of this type, the electrophotographic element is given a blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer owing to the substantial insulating property of the layer, i.e., the low conductivity of the layer in the dark. The electrostatic charge formed on the surface of the photoconducting layer is then selectively dissipated from the surface of the layer by exposure to light through a negative by a conventional exposure operation such as, for example, by a contact-printing technique, or by lens projection of an image, etc., to form a latent image in the photoconductive layer. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that light causes the charge to leak away in proportion to the intensity of the illumination in a particular area. The charge pattern remaining after exposure is then de-

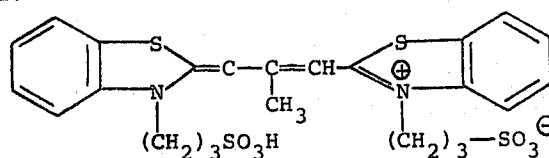
veloped, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust, i.e., powder, a pigment in a resinous carrier, i.e., toner, or a liquid developer may be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been described in the patent literature in such patents, for example, as U.S. Pat. No. 2,296,691, and the like. In process of electrophotographic reproduction such as in xerography, by selecting a developing particle which has as one of its components, a low-melting resin, it is possible to treat the developed photoconductive material with heat and cause the powder to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the image formed on the photoconductive layer can be made to a second support which would then become the final print. Techniques of the type indicated are well known in the art and have been described in U.S. Pat. Nos. 2,297,691 and 2,551,582 and in "RCA Review," Vol. 15 (1954), pages 469-484.

The present invention will be illustrated in greater detail in conjunction with the following specific example which sets forth a representative fabrication of the film units of the present invention, which, however, is not limited to the detailed description herein set forth but is intended to be illustrative only.

A dye sensitized gelatino silver halide emulsion comprising, for example, 8 percent silver halide measured as silver and 8 percent gelatin (weight basis) or such other ratio percent as shall be selected may be prepared by adding to a photosensitive silver halide emulsion, prepared as detailed above and comprising, for example, 9.5 percent silver halide measured as silver and 9.5 percent gelatin, at 38° C., an aqueous solution of a sensitizing dye adapted to provide the concentrations desired. To the resultant emulsion may then be added a dispersion of the orthorhombic lead monoxide semiconductor and sufficient water added to provide, for example, a 4.4 percent silver halide and 4.4 percent gelatin emulsion, or such other concentration as is selected, and the emulsion coated on a conventional transparent film base support for the further usage detailed.

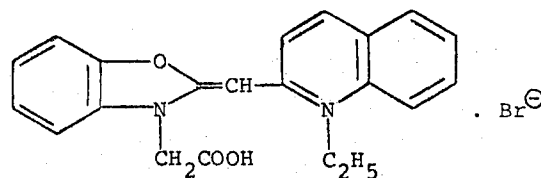
The specific sensitizing dyes selected to further illustrate hereinafter the present invention comprises the following with the class to which the dye belongs illustrated:

I.



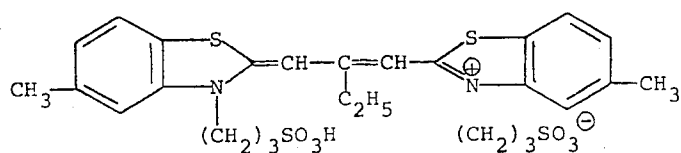
Thiocarbocyanine

II.



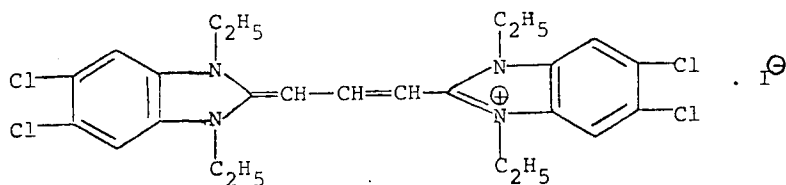
Oxa-2'-cyanine

III.



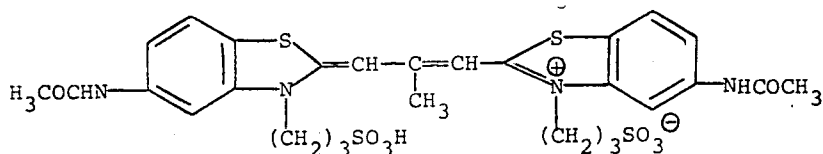
Thiacarbocyanine

IV.



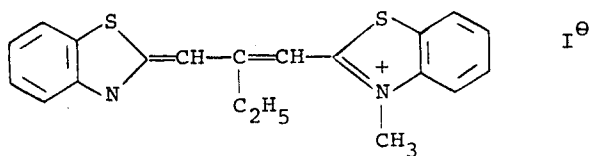
Benzimidazolocarbyanine

V.



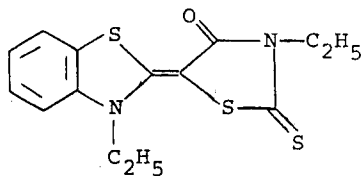
Thiacarbocyanine

VI.



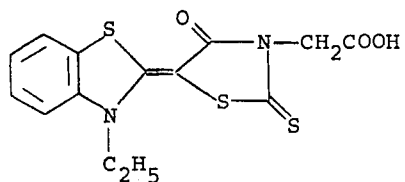
Thiacarbocyanine

VII.



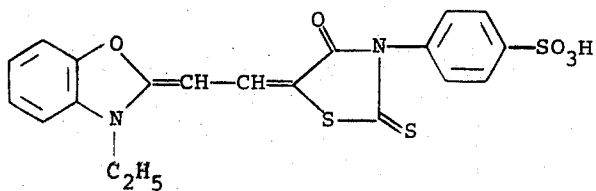
Apocyanine

VIII.



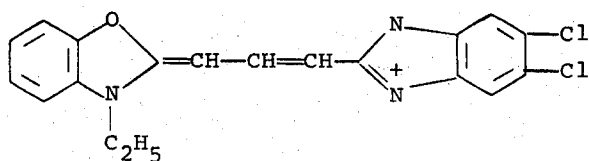
Apocyanine

IX.



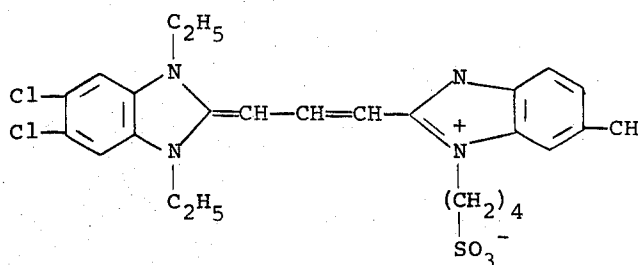
Merocyanine

X.



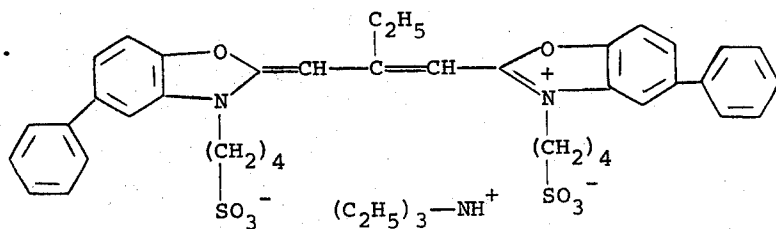
Benzimidazol-oxacarbocyanine

XI.



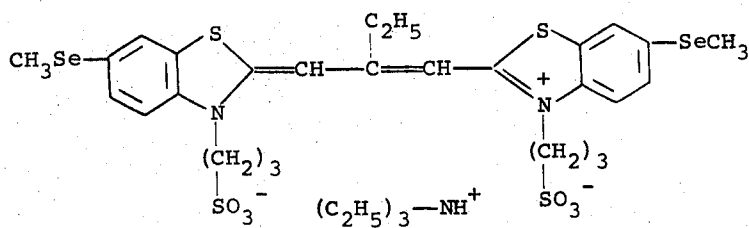
Benzimidazolocarbo-cyanine

XII.



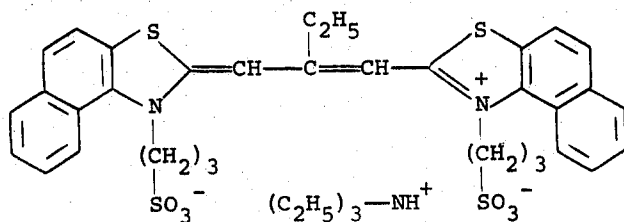
Oxacarbocyanine

XIII.



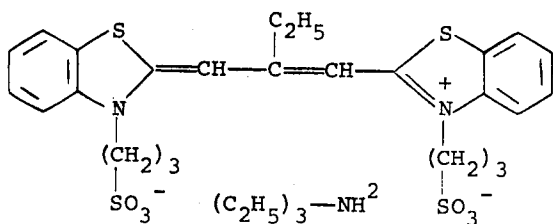
Thiocarbocyanine

XIV.



Thiocarbocyanine

XV.



The table set forth hereinafter specifically illustrates the advantages to be procured by means of the present invention and details the composition of and photographic results of emulsions prepared in accordance with the procedure detailed above.

Specifically, photosensitive elements prepared as set forth above were exposed in a step wedge spectrometer and processed in accordance with silver diffusion transfer processing techniques detailed above employing commercial Type 42 processing reagent and receiving element (Polaroid Corporation, Cambridge, Massachusetts, U.S.A.).

rated film sensitized with the sensitizing dye of Formula IV showed a one-half step increase when exposed and processed as described above.

The effectiveness of the introduction of the PbO semiconductor into a silver halide photographic system is graphically illustrated by referring to the figures. FIG. 1 is a graphic representation of the action spectra of a silver iodochlorobromide (about 3% I⁻, about 12% Cl⁻ and about 85% Br⁻) emulsion sensitized with about 4 mg. per gram of silver of the sensitizing dye of Formula I. FIG. 2 is the graphical representation of the action spectra of the same emulsion delineated in FIG. 1 except that the semiconductor in a mole ratio of about 5:1 (silver/orthorhombic PbO) was introduced into the emulsion. It will be noted that the action spectra shows a significant amplification with respect to incident radiation utilization for the formation of the silver image throughout the entire wavelength range.

In a further embodiment, the sensitizing dye and semiconductor were combined and then added to the silver halide emulsion. Unexpectedly, the action spectra indicated an amplified response both in the inherent

TABLE 1

Emulsion Composition	Sensitizing Dye and Level	(mg/g Ag)	PbO (moles/mole Ag)	Approximate Photographic Speed Results Compared to Control (No PbO)
AgCl	IV	1.0	1:1	1 stop increase
do.	IV	2.0	1:1	2 stops increase (sl. fog)
do.	XIII	1.0	1:1	1 stop increase (sl. fog)
do.	XIII	2.0	1:1	1 stop increase (sl. fog)
do.	XIII	4.0	1:1	2 stops increase (sl. fog)
do.	XIV	1.0	1:1	1 1/2 stops increase
do.	XIV	2.0	1:1	1 1/2 - 2 stops increase
do.	XIV	4.0	1:1	1 1/2 - 2 stops increase
AgBr	I	2.0	1:0.5	2 1/2 - 3 stops increase (sl. fog)
do.	I	4.0	1:0.5	3 stops increase (sl. fog)
do.	I	8.0	1:0.5	3 stops increase (sl. fog)
do.	I	2.0	1:0.25	3 stops increase (sl. fog)
do.	I	2.0	1:0.125	2 1/2 stops increase (u. sl. fog)
AgClBr (1% I, 12% Cl)	VI	1.6	1:0.5	1 stop increase
AgClBr (3% I, 12% Cl)	III	1.5		
	V	2.0	1:0.1	2 stops increase
AgClBr (3% I, 12% Cl)	III	1.5		
	V	2.0	1:0.2	3 stops increase
AgClBr (6% I, 12% Cl)	XV	3.0	1:0.25	1/2 stop increase
do.	XV	2.0		
	X	1.2	1:0.2	1 1/2 stop increase
do.	XV	2.0		
	X	0.80		
	XI	0.97	1:0.2	1/2 stop increase
AgBr	II	1.0	1:0.125	1/2 - stop increase
do.	II	2.0	1:0.125	1 stop increase
do.	II	4.0	1:0.125	1/2 stop increase
do.	IX	0.5	1:0.125	1/2 stop increase
do.	IX	1.0	1:0.125	1 stop increase
do.	IX	2.0	1:0.125	1 1/2 stop increase
do.	IX	4.0	1:0.125	2 stops increase
do.	IX	8.0	1:0.125	2 stops increase
do.	III	0.5	1:0.5	2 1/2 stops increase (sl. fog)
do.	III	1.0	1:0.5	2 1/2 stops increase (sl. fog)
do.	III	2.0	1:0.5	2 1/2 stops increase (v. sl. fog)
do.	III	4.0	1:0.5	3 stops increase
do.	III	8.0	1:0.5	3 1/2 stops increase
do.	VII	2.0	1:0.5	1 stop increase (v. sl. fog)
do.	VII	4.0	1:0.5	1/2 stop increase
do.	VIII	2.0	1:0.5	1 stop increase
do.	VIII	4.0	1:0.5	1/2 stop increase

Similar advantageous results were also achieved with test procedures employing a plurality of sensitizing dyes in replacement of the dyes denoted above and employing silver halide systems including binderless silver halide photosensitive elements; for example, employing a gel dispersion of PbO overcoated on an AgBr evapo-

region of silver halide absorption and in the spectrally sensitized region as compared to dye sensitization alone. It was also found that the sensitivity of an emulsion to which was added premixed dye and PbO semiconductor in the inherent region was greater than that of the original emulsion with no sensitization. This phe-

nomenon is particularly unexpected since spectral sensitizers are traditionally considered to cause at least a limited degree of desensitization in the inherent region of crystal photosensitivity.

The effectiveness of the premixed sensitizing dye and semiconductor is graphically illustrated by a comparison of FIG. 3 to FIGS. 1 and 2. FIG. 3 is a graphical representation of the action spectra of an emulsion of the same composition as FIG. 2 except that the sensitizing dye and the PbO were precombined prior to addition to the silver halide emulsion. It will be noted that with respect to the amplified response, such response is achieved in the inherent region of silver halide crystal absorption in addition and not to the detriment of that achieved in the region of spectral sensitization.

It should be understood that the present invention also contemplates the injection of additional electrons into the system as by the imposition of an electric current on the silver halide dye-semiconductor-containing emulsion. Such electron injection may be provided, for example, by imposing an electrical current onto a metal plate on which the emulsion layer is coated. Further amplification of the photosensitivity of the crystals to incident actinic radiation will be obtained.

It should also be understood that the present invention contemplates the application of a voltage to photosensitive elements during exposure. For example, this could be accomplished by employing a transparent electrode, such as Nesa glass, over the exposure surface.

Since certain changes may be made in the above product without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photosensitive element which comprises a particulate dispersion of silver halide crystals adapted to be reduced to silver upon contact with a silver halide reducing agent, as a function of said crystals' exposure to incident electromagnetic radiation actinic thereto, having associated therewith in electron donating relationship and sensitizing dye and an orthorhombic lead monoxide semiconductor, each of said dye and semiconductor adapted to donate electrons to said silver halide crystals as a function of the exposure of said element to incident electromagnetic radiation actinic to said element.

2. A photosensitive element as defined in claim 1 wherein said dye possesses a conduction band energy level above that possessed by said silver halide crystals.

3. A photosensitive element as defined in claim 2 wherein said silver halide crystals are selected from a group consisting of silver iodobromide and silver iodo-chlorobromide crystals.

4. A photosensitive element as defined in claim 2 wherein said dye is a cyanine sensitizing dye.

5. A photosensitive element as defined in claim 4 wherein said cyanine sensitizing dye is an optical sensitizing dye adapted to extend the range of the electromagnetic radiation spectrum to which said silver halide crystals are responsive.

6. A photosensitive element as defined in claim 1 which comprises a particulate dispersion of silver halide crystals adapted to be reduced to silver by contact

with a silver halide reducing agent, as a function of the exposure of said element to incident electromagnetic radiation actinic to said element, having associated therewith an electron donating cyanine sensitizing dye and a particulate dispersion of an orthorhombic lead monoxide electron donating semiconductor, each of said cyanine dye and semiconductor associated with said silver halide crystals in electron donating relationship and adapted to donate electrons to said silver halide crystals as a function of said exposure of said element to said incident electromagnetic radiation actinic to said element.

7. A photosensitive element as defined in claim 6 wherein said inorganic semiconductor is disposed in electron donating relationship with said cyanine dye and is adapted to donate electrons from said semiconductor to said dye as a function of the donating of electrons from said dye to said silver halide crystals upon exposure of said element to said incident actinic radiation.

8. A photosensitive element as defined in claim 7 wherein said cyanine dye is a spectral sensitizing cyanine dye adapted to extend the range of the electromagnetic radiation spectrum at which said silver halide crystals are responsive.

9. A photosensitive element as defined in claim 8 wherein said spectral sensitizing cyanine dye possesses a conduction band energy level above that possessed by said silver halide crystals.

10. A photosensitive element as defined in claim 9 wherein said semiconductor possesses a conduction band energy level above that possessed by said spectral sensitizing cyanine dye.

11. A photosensitive element as defined in claim 10 wherein said cyanine spectral sensitizing dye possesses a conduction band energy level above the conduction band gap energy level of said silver halide crystals.

12. A photosensitive element as defined in claim 11 wherein said semiconductor possesses a conduction band energy level above the conduction band energy level of said silver halide crystals.

13. A photosensitive element as defined in claim 10 wherein said silver halide crystals are selected from a group consisting of silver iodobromide and silver iodo-chlorobromide crystals.

14. A photosensitive element as defined in claim 13 wherein said silver halide crystals, said cyanine dye and said semiconductor are disposed in a polymeric matrix.

15. A photosensitive element as defined in claim 12 wherein said polymeric matrix comprises gelatin.

16. A photosensitive element as defined in claim 6 including associated therewith a silver halide developing agent.

17. A photosensitive element as defined in claim 6 including associated therewith a photographic diffusion transfer process image-forming material adapted to diffuse as a function of the exposure of said silver halide crystals to a receptor adapted to receive diffusion transfer process image-forming material diffusing thereto to provide to said receptor an image as a function of a point-to-point degree of the photosensitive element's exposure to said incident actinic radiation.

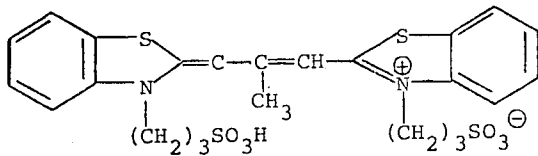
18. A photosensitive element as defined in claim 17 wherein said diffusion transfer process image-forming material comprises a diffusion transfer process dye image-forming material.

19. A photosensitive element as defined in claim 18 wherein said diffusion transfer process dye image-forming material is adapted to provide an imagewise distribution of diffusible dye as a function of the photo-exposed areas of said photosensitive element.

20. A photosensitive element as defined in claim 18 wherein said diffusion transfer process dye image-forming material is adapted to provide an imagewise distribution of diffusible dye as a function of the unexposed areas of said photosensitive element.

21. A photosensitive element as defined in claim 20 wherein said diffusion process dye image-forming material is a dye which is a silver halide reducing agent adapted to reduce silver halide crystals to silver as a function of the exposure thereof to provide an imagewise distribution of diffusible dye in terms of unexposed areas of said photosensitive element.

22. A photosensitive element as defined in claim 4 wherein said cyanine sensitizing dye is:



23. A photosensitive element which comprises a particulate distribution of photosensitive silver halide crystals having associated therewith sensitizing dye and a particulate dispersion of an orthorhombic lead monoxide semiconductor adapted to amplify the photosensitivity of said photosensitive crystals to incident actinic radiation.

24. A photosensitive element as defined in claim 23 wherein said photosensitive crystals exhibit increased photosensitivity to incident actinic radiation within the range of the electromagnetic radiation spectrum to which said crystals exhibit inherent sensitivity.

25. A photosensitive element as defined in claim 23 wherein said photosensitive crystals exhibit photosensitivity to incident actinic radiation within the range of the electromagnetic radiation spectrum to which said crystals exhibit no inherent sensitivity.

26. A photosensitive element as defined in claim 25 wherein said photosensitive crystals exhibit photosensitivity throughout the visible electromagnetic radiation spectrum.

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