United States Patent

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[72] Inventors **George R. Bird**
Concord;
Alan E. Rosenoff, Waltham, both of Mass.

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[73] Assignee **Polaroid Corporation**
Cambridge, Mass.

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[54] **PHOTORESPONSIVE ARTICLES COMPRISING PSEUDO-POLYMERIC SPECTRAL SENSITIZATION SYSTEMS**
24 Claims, No Drawings

[52] **U.S. Cl.** **96/1.7,** 260/240.1, 96/1.6, 96/124, 96/126, 96/127, 96/128, 96/137

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[50] **Field of Search** 96/1, 1.5, 1.7, 104, 105, 124, 126, 127, 128, 137; 260/240.1

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Primary Examiner—George F. Lesmes
Assistant Examiner—John C. Cooper, III
Attorneys—Brown and Mikulka and Sheldon W. Rothstein

ABSTRACT: Photoresponse of a given photosensitive element is enhanced by utilizing a spectral sensitization system adsorbed to said photosensitive element, said system comprising a layer of spectral sensitizing dye material comprising nonrepetitive segments, each of said segments more distal from said photosensitive element than the preceding segment possessing a higher intrinsic energy absorption frequency range than the energy absorption frequency range of the immediately preceding segment, and an intrinsic energy transmitting frequency range which overlaps the energy absorption frequency range of the next preceding segment thereby providing a radiationless circuit capable of transmitting photon-excitation-derived energy to said photosensitive element.

PHOTORESPONSIVE ARTICLES COMPRISING PSEUDO-POLYMERIC SPECTRAL SENSITIZATION SYSTEMS

The instant application is a continuation-in-part of U.S. application Ser. No. 438,124 of George R. Bird and Alan E. Rosenoff, filed Mar. 8, 1965, now abandoned.

The present invention relates to processes particularly adapted to provide photoresponsive devices possessing greater propensities for absorption of incident energy than had been heretofore possible.

In accordance with techniques disclosed in the art, photoresponsive crystal devices and particularly photoresponsive silver halide crystal devices 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 photoresponsive crystal, and particularly a photoresponsive silver halide crystal, 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 III of the Periodic Table of Elements and have an atomic weight greater than 100, for example, potassium chloroplatinate, sodium chloropalladite, ammonium chlorohodinatoe, and the like, in amounts below that which produces any substantial fog inhibition, as described in U.S. Pat. No. 2,448,060; gold salts, for example, potassium aurothiocyanate, potassium chloroaurate, 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, described in U.S. Pat. No. 2,487,850; polyamines such as diethyltriamine, as described in U.S. Pat. No. 2,518,698; and spermine, as described in U.S. Pat. No. 2,521,925; or bis-(aminoethyl)-sulfide and its water-soluble salts, as described in 2,521,926, individually or in combination. Such chemical sensitization procedure provides increased response to electromagnetic radiation by the photoresponsive silver halide crystal 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 photoresponsive crystal, and particularly a photoresponsive silver halide crystal, 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 surfaces of the crystal 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 a silver halide crystal see Hammer, F. M., *The Cyanine Dyes and Related Compounds.*

Photographic action may be considered to be the photographic results observed upon transfer of an electron or energy stimulus to a photosensitive material, e.g., a photosensitive silver halide crystal. In practice, it may be measured by an evaluation of the degree of blackening produced in a given photosensitive material by a stimulus, as above denoted, which renders individual silver halide grains developable. The stimulus which alters the characteristics of the photosensitive material to render it developable is transferred to the photosensitive material either directly from incident electromagnetic radiation or from a dye aggregate adsorbed to said photosensitive material. Such photographic action is a function of both the amount of quanta, or stimulus, absorbed, and the relative quantum efficiency of the absorbed quanta in the system. Stated differently, it may be considered to be a function of the stimulus absorptive propensity of a photoresponsive system, and of the efficiency of the system in utilizing the absorbed stimulus to render photosensitive material developable. For purposes of the instant treatment, quantum efficiency is considered to be a measure of the quanta which initiate photochemical changes relative to the total quanta absorbed by a spectrally sensitized photosensitive system. A quantum efficiency less than 1, for example, would indicate that some absorbed quanta were not effective to produce the desired reaction.

By the invention disclosed herein, an increase in the quantum absorptive propensities of a spectrally sensitized photosensitive system has been achieved while experiencing relatively little, if any, deleterious effect on the quantum efficiency of said system.

It is a principal object of the present invention to provide new, improved and simplified procedures, particularly adapted to provide photoresponsive elements possessing increased energy absorptive propensities and, particularly, photoresponsive silver halide crystals possessing improved electromagnetic and photon-excitation-derived energy response due to increased energy absorption.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

By means of the traditional procedures disclosed in the art as adapted to accomplish spectral sensitization of a photoresponsive crystal, and preferably sensitization of a photoresponsive silver halide crystal, a cyanine dye in the form of polymeric aggregates is aadsorbed to the receptive faces, or surfaces, of the crystal in a statistical monomolecular layer thickness or less. Specifically, the cyanine dyes employed for purposes of photoresponsive crystal 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 each heterocyclic ring. Adsorption is generally believed to be partly accomplished by an unknown type of chemisorption between negative crystal surface charges provided, for example, by the excess halide components of the silver halide crystal, and the positive charge of the cyanine chromophore. Adsorption is also favored by the ability of the dye to form silver complexes at the surface of the crystal with one or more ligand bonds between hetero atoms of the cyanine system and silver ions bound to the crystal surface.

It has also been traditionally found that the efficiency of the spectral sensitization of a, for example, silver halide crystal increases in accordance with an increase in the chemisorption 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 the increase in sensitivity peaks or plateaus. Specifically, maximum sensitization has been found ordinarily 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. As a matter of fact, the concentration of dye at optimum spectral sensitization usually is reached just short of monomolecular coverage of the crystal surface.

Sensitivity conferred by a sensitizing dye does not increase proportionately to the concentration of the dye, but rather passes through a maximum as concentration is increased. Note U.S. Pat. No. 2,688,545. 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: Hammer, F. M., *The Cyanine Dyes and Related Compounds* and Borin, A. V., *Investigation of the Concentration Effect in Optical Sensitization of Photographic Emulsions*, Uspekhi Nauch. Fab. Akad. Nauk. SSSR, Otdel. Ihim. 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. It will be accordingly appreciated that within the context of the above discussion, merely piling layer upon layer of dye upon the crystal will not improve the sensitivity above the plateau region unless the herein described novel energy transmission circuit is utilized.

The energy or charge-carrier absorptive propensity of a photoresponsive element comprising a plurality of crystals 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 crystal. The aforementioned monomolecular layer adsorption of the dye to the appropriate surfaces of the crystals fails, by a relatively large degree, to provide complete adsorption 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, in the order of about 7 microns in thickness, and including a dispersion of photoresponsive silver halide crystals 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 7 percent of the total incident radiation. W. West & V. I. Saunders, *Wissenschaftliche Photographie*, W. Eichler, H. Frieser and O. Helwich, eds., Verlag Dr. O. Helwich, Darmstadt, 1958, P. 48. Since the above incompletely absorbing system is already sensitized to peak response, the next response of the system cannot be improved by simply adding more of the same sensitizing dye.

The decrease in sensitivity experienced by increasing the number of layers of dye adsorbed on the adsorbing surfaces of the crystal above the concentration level required to provide optimum sensitization is the result of a concomitant plurality of interrelated effects. Among such effects are increased aggregation of dye in aggregates which are unable to transfer charge-carriers or energy to the crystal, and which aggregates compete for adsorption sites on the crystal's adsorbing surfaces with effective sensitizing dye, or dye aggregates, capable of effecting energy transfer. In addition, in extreme situations, such aggregates may positively, and effectively, mask sensitivity itself, or selected sensitivity frequencies, which would ordinarily have been provided by the dye adsorbed in the absence of such aggregates. In addition, the catastrophic results of exceeding, concentrationwise, the plateau or peak region of optimum sensitivity is probably, in part, the result of the formation of a multimolecular layer coverage of dye, on at least a portion of the crystal's adsorbing surfaces, whereby the dye molecule of the multimolecular layer next adjacent the adsorbing surface possesses, by reason of crystal influence, a lower energy absorption wavelength maximum than the energy absorption wavelength maximum of the second and succeeding dye molecules spatially removed from the crystal's surface and contiguous the dye molecule adsorbed on the crystal surface. Thus, where the energy transmission, or fluorescence emission, bands of the dye molecule adsorbed on the surface of the crystal overlap the absorption bands of the succeeding dye molecules in order of increasing wavelengths of absorption in the direction away from the crystal surface, energy developed by photon excitation irreversibly transfers in the direction away from the photoresponsive crystal, depriving the crystal of the energy necessary for response. This is in accord with the Forster theory of radiationless energy transfer, and with the experimental work of H. Kuhn et al.; see: Theodor Forster, *Fluoreszenz Organischer Verbindungen*, pp. 83–84; M. M. Zwick u. H. Kuhn, Z. Naturforschung 17*a*, 411 (1962); and K. H. Dnexhage, M. M. Zeick u. H. Kuhn, Ber. d. Bunsenges. f. physikal. chemie 67, 62 (1963). It will be readily appreciated that even a limited occurrence of sites, on the crystal's adsorbing surface, having such detrimental multimolecular layer dye coverage will provide an extremely efficient mechanism for short circuiting the desired pathway of energy transfer toward the crystal. Not only is there then present and accupying active sites on the photoresponsive crystal's adsorbing surface, a dye composite which by structure cannot transfer energy toward the crystal, but, in addition, the dye structure provides a mechanism for conducting energy from the contiguous monomolecular layer situated dye, away from the photoresponsive crystal. Most of the current literature views the loss of blue speed at high dye concentrations as being due to chemical desensitization by the dye—but here we propose a second mechanism which would degrade the sensitized speed and may have some undesirable effect on the blue speed.

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 adsorbing 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-derived-excitation energy quantum efficiency. However, the technique merely makes a relatively "good" cyanine dye optical sensitizing agent from a relatively "poor" sensitizer and the combined effective concentrations generally cannot exceed that which provides the previously described monomolecular layer coverage, or less, while still providing maximum sensitization.

It has been disclosed and claimed in U.S. Pat. application of George R. Bird and Alan E. Rosenoff, Ser. No. 804,254, filed Mar. 4, 1969, that an increased response due to a greater absorption of incident energy may be provided to a photoresponsive crystal, and particularly to a photoresponsive silver halide crystal, by a technique which comprises adsorbing a plurality of energy absorbing and transmitting components, in layer relationship, on the receptive surfaces, or faces, of the photoresponsive crystal, wherein the component adsorbed immediately to the crystal surface comprises a layer of an optical sensitizing agent and preferably a cyanine sensitizing dye, present in a concentration which provides maximum sensitization, and each succeeding layer comprises a layer of a component having energy transmitting, or fluorescence emission, bands, at least in part, overlapping the energy absorption bands of the preceding component and situated in order of progressively decreasing wavelength ranges of absorption, respectively, in the direction away from the crystal surface. Optimal efficiency in circuiting photon-excitation-derived energy to the crystal, it is disclosed, will be achieved when the layers comprising the spectral sensitization system are about monomolecular since energy losses due to internal effects within discrete layers of different materials will be minimized.

Specifically, in the preferred mode of the invention of the above-denoted application a photoresponsive element is provided having a multimolecular layer adsorbed to the receptive surfaces, or faces, of the element, wherein the multimolecular layer comprises, in order from the crystal surface, about a monomolecular layer of a cyanine spectral sensitizing dye and a supersensitizer therefor, which provides optimum photographic sensitivity, and at least one layer of an energy absorbing and transmitting material, the latter layer(s) also preferably comprising a cyanine spectral sensitizing dye, and each of the layers having a photon-excitation-derived energy absorption frequency range at a higher frequency than the energy absorption frequency range of the next preceding layer from the crystal surface and, in the case of all layers but the

layer contiguous the crystal surface, having an energy transmitting, or fluorescence emission, frequency range which overlaps the energy absorption frequency range of the next preceding layer, to provide thereby a circuit capable of transmitting photon-excitation-derived energy to the crystal.

The total frequency range of absorption provided by a composite multimolecular layer as described above will comprise the sum of the absorption frequency ranges of the individual components and may thus be tailored, by suitable component selection, to envelop, or cover, any specific frequency range of electromagnetic radiation desired. It will also be appreciated that each of the components receiving transferred energy will accommodate and respond to incident electromagnetic radiation in addition to the photon-excitation-derived energy transferred to and through the individual component from other constituents of the multilayer structure.

It will be recognized that the energy circuit utilized in a photographic environment as claimed the above-denoted Bird and Rosenoff application is predicated upon a critical relationship between discrete layers of different energy absorptive and conductive materials wherein each subsequent material in a direction distal from the photosensitive element surface has an energy absorption frequency range which is higher than the energy absorption frequency range of the material next proximal the photosensitive element and an energy transmission frequency range which overlaps the energy absorption frequency range of the said next proximal material. Under ideal conditions the attainment of the proper layerwise relationship between the strata comprising the above-denoted energy conductive circuit is assured, principally when only a few strata are utilized, ty e.g. two or three and particularly when the material comprising the energy circuit is applied to an orderly structured photosensitive element such as a single crystal, a binderless silver halide layer, etc.; or when the ingredients comprising the energy circuit are so uniquely related as to assure the proper relationship each to the other. In the latter instance, the unique relationship may be in the form of tenacious adsorption to silver halide, preferential intramolecular attractions between various components, etc. It will be appreciated that in certain instances, as, for example, when the constituents of the energy circuit are added to a silver halide dispersion comprising randomly sized, shaped and oriented silver halide grains, depending upon the particular components and their relative affinities for one another and/or the photosensitive grains, achievement of a predetermined stratified relationship between the materials forming the energy circuit may approach a statistically random sequence and actually conduct energy in a direction away from the photosensitive element in derogation of the purpose for which such a circuit is utilized.

It has been found that the above-denoted problems pertaining to the assurance of a predetermined stratified configuration of an energy conductive circuit adsorbed onto a photosensitive medium may be eliminated by synthesizing the desired spectrally sensitizing energy conducting circuit in a chemically associated form prior to adsorption thereof to the photosensitive element. Viewed in isolation then; the energy conducting circuit will comprise a pseudopolymeric compound wherein each monomeric segment differs structurally from any other monomeric segment and possesses an absorption frequency and transmission range relationship to the other monomeric segments of the compound as detailed in the above-denoted Bird, et al. application and as more fully described below. It will be accordingly recognized that the present invention will provide for the conduction of energy to an adsorbed photoresponsive element through a pseudopolymeric circuit comprising segments possessing intrinsic energy absorption and transmission frequency ranges which provide a radiationless path through said circuit in the direction of said adsorbed photoresponsive element.

As used herein the term "pseudopolymeric compound" is descriptive of a chainlike compound comprising a multiplicity of discrete segments at least one end of said compound comprising a cyanine spectral sensitizing segment possessing a given energy absorption and transmission frequency range and said segment(s) subsequent to said initial cyanine sensitizing dye segment possessing intrinsic energy absorption frequency range(s) in ascending order therefrom, each of said subsequent segments possessing intrinsic energy transmission ranges which overlap the energy absorption frequency range of the next preceding segment. Ideally the pseudopolymeric compounds of the present invention will be branched or preferably bridged compounds and will comprise either two or three segments.

In addition, within the context of the present invention and unless otherwise specified, the term "segment" is considered to define a link in a pseudopolymeric compound chain which, in relation to other such links in the chain, possesses the above-denoted relative energy absorption and transmission characteristics.

Although the monomeric segment of the pseudopolymeric compounds utilized in the present invention which comprises one end of the monomeric structure and is adsorbed directly to the photosensitive element and will comprise the longest wave length absorption component of the pseudopolymeric circuit must be a spectral sensitizing agent, there is no specific requirement that any one or more of the remaining components themselves be spectral sensitizing agents—although in the preferred embodiment they will be so constituted—but merely that they possess the intrinsic capability of transferring photon-excitation-derived energy by means of the herein described circuit without imparting any deleterious effects to the photographic system in which they are incorporated. Ideally, the segments comprising the pseudopolymeric compositions of the present invention will be substantially planar in character, and be capable of fluorescence, as, for example, cyanine dyes, hydrocarbon dyes, etc., to easily facilitate aggregate formation on the photosensitive element. Azo dyes, however, should not be utilized since they inherently dissipate absorbed energy internally while transmitting little of the energy requisite for the proper operation of the energy transfer mechanism of the instant invention and severely effect the efficiency thereof.

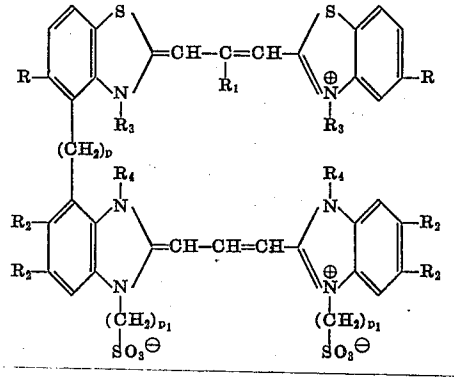
Within the context of the present invention, it will, therefore, be appreciated that the mechanism of attachment of the segment which it is proposed be directly adsorbed to the photosensitive element be preferential with respect to any and all other segments present in the pseudopolymeric system. Such preferential adsorption is preferably achieved by tailoring the psuedopolymeric material so that the functionally adsorptive area of the pertinent segment possesses the strongest adsorptive propensity to the photosensitive element. It is generally regarded that the most tenaciously adsorbed cyanine dyes to photosensitive silver halides comprise selenazoles with thiazoles, oxazoles, imidazoles, etc., following in descending order by the ligand bonding mechanism described above. In order to assure the proper dye relationship relative to the photosensitive element, it has additionally been found advantageous to impart to the pseudopolymeric molecule end most distal from the photosensitive element a substituent or substituents which inherently retard adsorption of said end to said photosensitive element. Among such substituents are groups which provide a steric effect, such as, carbon chains of at least four members and preferably eighteen members or more, aryl groups, and groups which provide electronegativity to said distal end, such as, $PO_3^{-7E^-}$, $SO_3^{-7E^-}$, $CO_2^{-7E^-}$, etc. Most preferably, it is suggested that steric groups which additionally contain an electronegative substituent, as described above, be utilized.

It will further be appreciated that within the context of the present invention the pseudopolymeric segments intermediate the longest and shortest wavelength absorptive segments must possess adsorptive propensities toward the photosensitive element in a substantially lesser degree than the said lowest wave length adsorptive segment in order to substantially assure that the dye will attach to the photosensitive element at the

predetermined end and will not be adhered through one of the intermediate monomeric segments. The spectrally sensitized photosensitive material of the present invention may thus be likened to a element containing a multiplicity of protuberances in the form of dye aggregate components projecting therefrom. It will be recognized that the fact that the pseudopolymeric materials of the present invention are adsorbed as aggregates, according to accepted spectral sensitizer adsorption theory, rather than as discrete molecules, additionally stimulates the proper orientation of the respective aggregate components on the photosensitive element and impedes adsorption of any but the preferentially adsorptive initial segment. See the Resolved Spectra of Small Cyanine Dye Aggregates and a Mechanism of Supersensitization, Rosenoff, Norland, Ames, Walworth and Bird, *Photographic Science and Engineering*, Vol. 12, No. 4 P. 185, 1968.

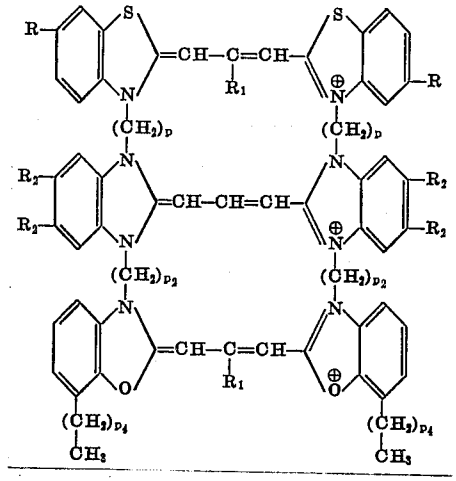
As has been aforementioned, the technique of supersensitization has the effect of taking a relatively poor spectral sensitizing compound and making a relatively good sensitizer out of it. As such, the supersensitizing component may be regarded as increasing the quantum efficiency of the photosensitizer out of it. As such, the supersensitizing component may be regarded as increasing the quantum efficiency of the photosensitive system. It is possible, and is in fact encouraged within the present invention, to utilize a supersensitizing composition in conjunction with the pseudopolymeric sensitizing agent. In keeping within the theory of supersensitizer activity set forth in the above-denoted Rosenoff et al. paper, best results will be obtained when the supersensitizer is added concomitantly with the addition of the primary spectral sensitizing agent which, in this case, is the above-denoted pseudopolymer, to the photosensitive material; however, satisfactory results may be attained by adding the supersensitizer either before or after the addition of the primary sensitizer.

The pseudopolymeric compositions of the present invention preferably comprise branched or bridged pseudopolymers as has been alluded to herein. In the case of branched pseudopolymeric materials the problem of coiling is substantially nonexistent due to the inherent molecular rigidity and aggregation of the material and such compounds should be useful in chain lengths substantially as long as the operator may desire, provided segments subsequent to the adsorbed high wave length range absorbing segment do not contain tenacious photosensitive element adsorptive components. An exemplary generic structure of certain of such compounds is reproduced below.



where R is hydrogen, chlorine or methoxy; R_1 is hydrogen, methyl or ethyl; R_2 is hydrogen or chlorine; R_3 is methyl or ethyl; R_4 is methyl or ethyl; p is a positive integer between 3 and 10; and p_1 is a positive integer between 2 and 30.

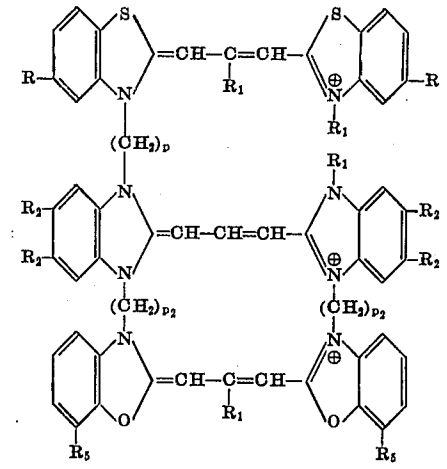
The second type of pseudopolymer, and the one most preferred for use herein, is the bridged or ladder polymeric material, wherein each segment is rigidly supported by each other segment through two attachment points. This structure is considered to be the most rigid and provides the best results in the environment of the present invention. Some exemplary compounds of this type are structurally reproduced below:



where R, R_1, R_2, R_3, and p are as indicated above; p_2 is a positive integer between 3 and 10; and p_4 is a positive integer between 2 and 30.

It should be noted that included within the context of the instant invention are unbranched linear pseudopolymeric materials. In general, the utilization of compounds of this type will produce the energy circuiting functionality toward which the instant invention is directed in a photographic environment. However, due to possible stereoisometric effects such compounds are not as efficient as the branched or bridged pseudopolymers described above since the bond structure of such compounds may not sufficiently restrict the movement of the energy circuit to its proper orientation on the photosensitive element.

Further included within the context of the present invention are pseudopolymeric compounds comprising both bridged and branched linkages throughout its structure as exemplified by the following structural formula:

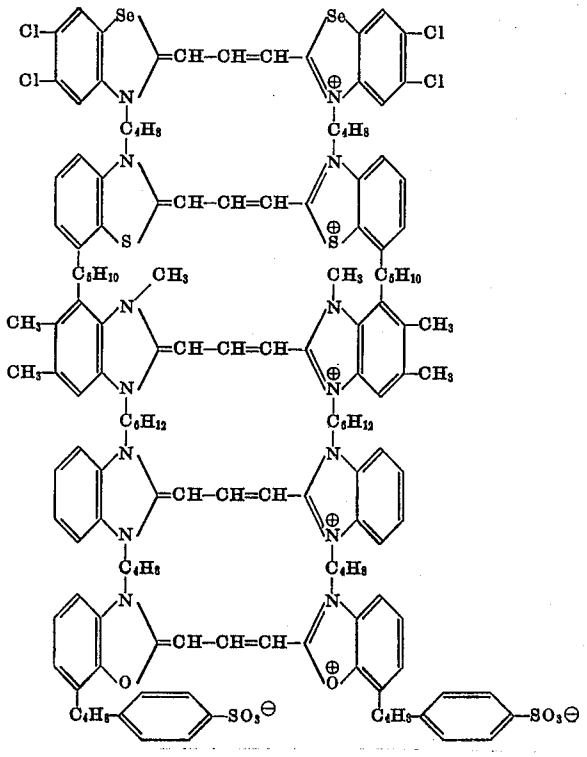


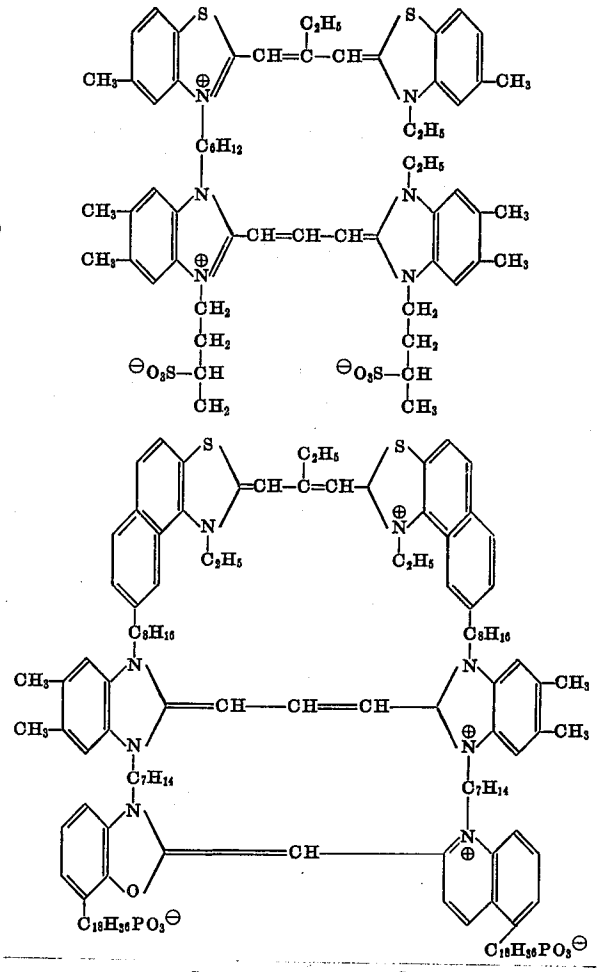
wherein R, R_1, R_2, p, and p_2 are as indicated above and R_6 is alkyl containing between five and 30 carbon atoms, or aryl, or aryl-substituted alkyl.

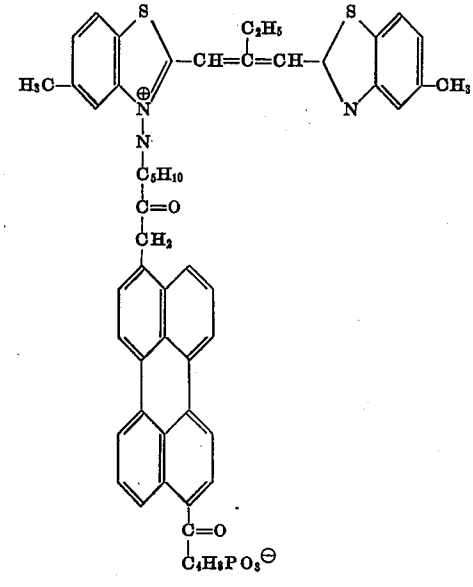
It will be noted from the compounds depicted above that the respective segments may be bonded, each to the other, by various groups. Most preferred for utilization in intersegmentary joinder are alkylene groups; however, it is emphasized that any group which is capable of providing the requisite segment joinder without providing deleterious effects to the system may be employed. Joinder of the various segments is accomplished by techniques known to the chemical synthesis art. Accordingly, the choice of joinder groups would be at the option of the operator. Such joinder may be accomplished by joining heterocyclic nitrogen atoms of separate segments through bivalent hydrocarbon groups or may be accomplished through other nuclear atoms or substituent groups. In the preferred case of cyanine dyes, joinder through the conjugated carbon chain is generally contraindicated due to the possibility of shifting segmentary spectral response.

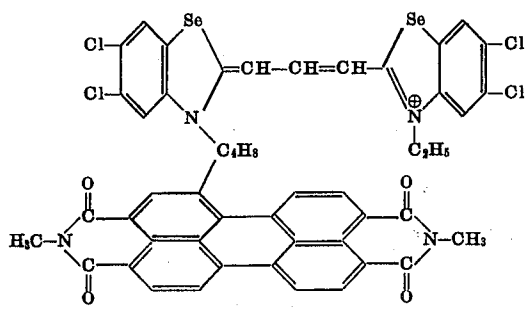
In the interest of efficiency it is encouraged that the relative distances between the segments of the pseudopolymeric compounds of the present invention be no more than about 100 A. from one another which provides a reduction in efficiency of radiationless energy transfer of about 50 percent over intimately arranged segments. For all practical purposes, the absolute outside limit of the distance between segments is 200 A. which reduces transfer efficiency by about 98 percent, which might be desired for certain very limited applications. Accordingly, the total length of any linking group will have to be considered in terms of system efficiency in providing the desired energy circuit for photographic utilization. For reference purposes, an alkylene connecting group containing three carbon atoms will be about 7 A. in length. It will additionally be appreciated that the point of attachment of linking groups on respective segments will also be effective in determining segmentary distances since nuclear and extranuclear attachment points will bear different spatial relationships toward adjacent segments of the pseudopolymeric compound.

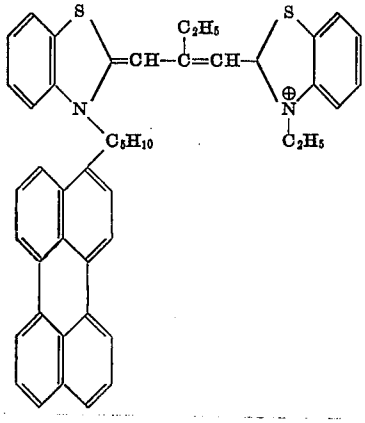
Exemplary of the numerous pseudopolymeric materials which may be utilized in the context of the present invention are:

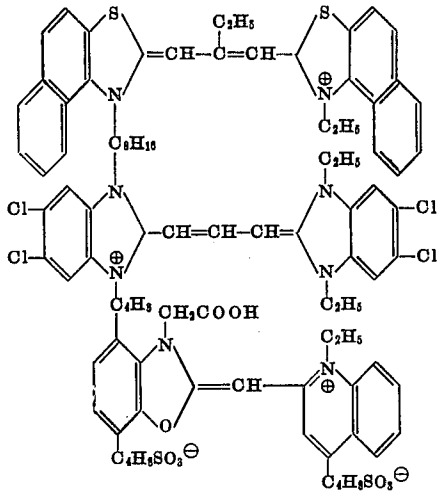


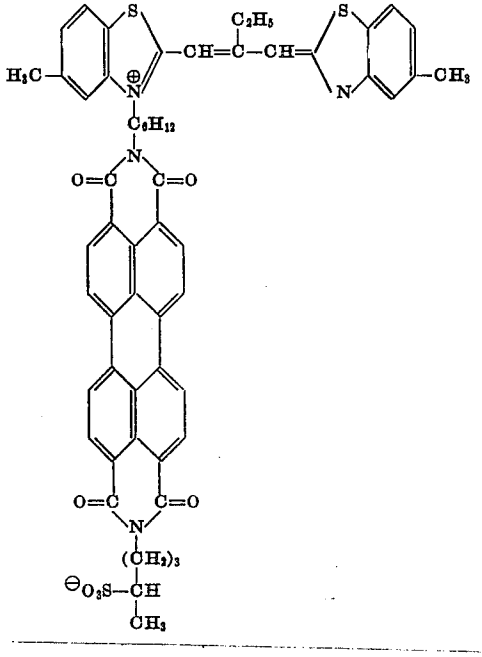








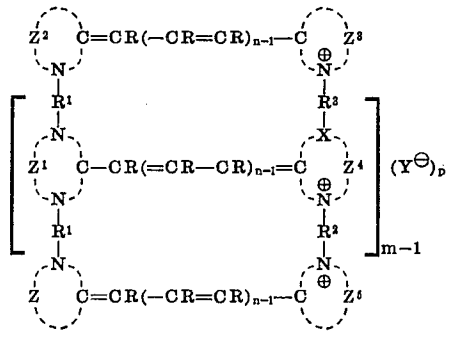




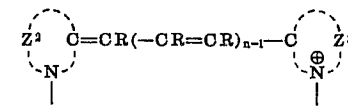
The above listing of compounds is considered to be exemplary only and not limiting. Evidently, within the bounds of the present invention, the number of possible pseudopolymeric compounds which may be utilized is, for all practical purposes, limited only by the desires of the operator.

Certain di- and trisegmented bridge-bonded pseudopolymeric cyanine optical sensitizing dyes comprising branched linkages and particularly adapted for employment in the fabrication of the subject photoresponsive elements may be visualized with reference to the formula:

(A)



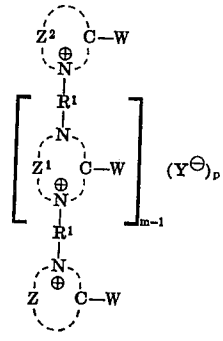
wherein m is 1 or 2; each n is 1, 2 or 3; R is hydrogen or a monovalent hydrocarbon group such as an alkyl or aryl group, preferably a lower alkyl group containing from one to four carbon atoms, a phenyl or a benzyl group, in the meso position of the methine chain, each R^1 may be the same or different and each is a divalent hydrocarbon group, preferably an alkylene group containing from two to six carbon atoms; X is a carbon, oxygen, selenium, sulfur, or nitrogen atom; R^2 is R^1, R or hydrogen in number satisfying the outstanding valence bonds; R^3 is R^2, when X is a nitrogen atom, or hydrogen satisfying the outstanding valence bonds designated; Z^1 represents the atoms necessary to complete a heterocyclic ring system of the imidazole series; each Z, Z^2, Z^3, Z^4, and Z^5 represents the atoms necessary to complete a heterocyclic nitrogen ring system, preferably a 5-or 6-membered thiazole, selenazole, oxazole, imidazole, thiazoline, quinoline, pyridine, or indolenine heterocyclic nitrogen ring system; Y represents an anion; and p represents a positive integer equal to the next number of Θ charges, wherein the segment



possesses a photon-excitation-derived energy absorption frequency range at a higher frequency than the energy absorption frequency range of the next adjacent segment and an energy transmitting frequency range within the energy absorption frequency range of said next adjacent segment, which segment, when m is 2, in turn, possesses a photon-excitation-derived energy absorption frequency range at a higher frequency than the energy absorption range of the remaining, or terminal, monomeric cyanine dye segment, and wherein the photoresponsive element adsorption potential of the terminal dye segment exceeds that of the preceding monomeric cyanine dye segments.

One method of preparing dyes of formula (A) comprises condensing a bis- or tris-cycloammonium quaternary salt of the formula:

(B)



wherein each W constitutes a reactive group capable of cyanine dye condensation, preferably a reactive group conventionally employed in the cyanine dye art, most preferably an active methyl or hydrocarbon mercapto group in one of α and γ positions with respect to a nitrogen atom of the associated heterocyclic ring system; as follows:

1. Directly condensing, in the presence of acetic anhydride and amyl nitrite, where W=methyl, or triethylamine and acetic anhydride, where W is a hydrocarbon mercapto, a cycloammonium quaternary salt of formula (B) to provide a dye of Formula (A), wherein n is 1, X is a nitrogen atom, R^2 and R^3 each=corresponding R^1, $Z=Z^5$, $Z^1=Z^4$, and $Z^2=Z^3$;

2. Condensing, in the presence of a basic condensing agent, two different cycloammonium quaternary salts of formula (B), wherein each W of one salt is methyl and each W of the second salt is hydrocarbon mercapto, to provide a dye of Formula (A), wherein n is 1, X is a nitrogen atom, R^2 and R^3 are R^1, and $R^{\text{least one of } R,\ R^1}$, Z, Z^1 and Z^2 differs from one of corresponding R^2, R^3, Z^5, Z^4 and Z^3;

3. Condensing, in the presence of a basic Condensing, agent, a cycloammonium quaternary salt of formula (B) with an ester of an orthocarboxylic acid to provide a dye of Formula (A) wherein n is 2, X is a nitrogen atom, R^2 and R^3 each equal corresponding R^1, $Z=Z^5$, $Z^1=$, $Z=4$, and $Z^2=Z^3$;

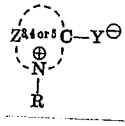
4. Condensing, in the presence of a basic condensing agent, a cycloammonium quaternary salt of formula (B) with an amidine such as N,N-diphenylformamidine, and the like, or, in the absence of a base, with an ester of an orthocarboxylic acid and then condensing the resultant product, in the presence of a basic condensing agent, with a different cycloammonium quaternary salt of formula (B) to provide a dye of formula (A), wherein n is 2, X is a nitrogen atom, R^2 and R^3 are R^1, and at least one of R, R^1, Z, Z^1 and Z^2 differs from one of corresponding R^2, R^3, Z^5, Z^4 and Z^3;

5. Condensing, in the presence of a basic condensing agent, a cycloammonium quaternary salt of formula (B) with a β-arylaminoacrolein anil salt or a 1,1,3,3-tetraalkoxypropane to provide a dye of formula (A) wherein n=3, X is a nitrogen atom, R^2 and R^3 each equal corresponding R^1, $Z=Z^5$, $Z^1=Z^4$, and $Z^2=Z^3$;

6. Condensing, in the absence of a basic condensing agent, a cycloammonium quaternary salt of formula (B) with a β-arylaminoacolein anil salt and then condensing the resultant product, in the presence of a basic condensing agent with a different cyaloammonium quaternary salt of formula (B) to provide a dye of formula (A) wherein n=3, X is a nitrogen atom, R^2 and R^3 are R^1, and at least one of R, R^1, Z, Z^1, and Z^2 differs from one of corresponding R^2, R^3, Z^5, Z^4 and Z^3;

7. Condensing, in the presence of a basic condensing agent, a cycloammonium salt of formula (B) with a cycloammonium salt of the formula:

(C)



wherein each W of one salt is a methyl group and each W of the second salt is a hydrocarbon mercapto group, preferably in a 1:2 mole ration, when m is 1, and a 1:3 mole ratio when m is 2, to provide a dye of formula (A) wherein n is 1, R^2 and R^3 is R or hydrogen and Z^3, Z^4 and Z^5 are equal to each other and may be equal to one or more of Z, Z^1 and Z^2;

8. Sequentially condensing according to the procedure of section (7), wherein at least two of Z^3, Z^4 and Z^5 are different, in order of reactivity with corresponding Z, Z^1 and Z^2, selected, in stoichiometric mole ratio necessary to provide reaction at the specific number of reaction sites desired, to provide a dye of formula (A) wherein n is 1, R^2 and R^3 are R or hydrogen, and at least two of Z^3, Z^4 and Z^5 differ from each other;

9. Condensing according to the dual step procedure of section (4), employing the cycloammonium compounds of section (7), or the compounds and sequential procedure of section (8), and including optional selection of specific cycloammonium compound to undergo the initial step of the section (4) procedure, to provide dyes of formula (A) wherein n is 2, R^2 and R^3 is R or hydrogen, and Z^3, Z^4 and Z^5 are the same or different; and

10. Condensing according to the dual step procedure of section (6), employing the cycloammonium compounds of section (7) or the compounds and sequential procedure of section (8), and compounds optional selection of a specific cycloammonium compound to undergo the initial step of the section (6) procedure, to provide dyes of formula (A) wherein n is 3, R^2 and R^3 are R or hydrogen, and Z^3, Z^4 and Z^5 are the same or different.

It will be apparent that the $Z^{0,1,2,3,4 \text{ and } 5}$ components of the intermediate cycloammonium quaternary salts will be selected with the requisite color values, or spectral absorption characteristics, as to provide formation of the desired compound possessing the spectral absorption and energy transmitting characteristics, detailed above, in order to effect the described energy transfer and selective absorption.

In addition, when the chosen synthetic procedure provides a mixture of products, separation of the desired dye from the mixture will be accomplished by the conventional procedures known in the art as particularly adapted to effect such separation, such as crystallization, electrophoresis, chromotography and the like.

In order to further insure that adsorption of the selected material occurs in the manner detailed above, as more fully discussed hereinbefore, components $Z^2$and Z^3 may preferably possess one or more steric and/or electronegative substituents, for example, sulfoalkyl, carboxyalkyl, sulfoalkyloxyalkyl, and the like, referred to hereinbefore, in order to insure that the pseudopolymer goes down on the crystal in the proper order. Since it is understood that the dye is adsorbed to a negative crystal surface, making one end of the dye more negative than the other end further insures proper adsorption on the crystal surface.

As examples of esters of an orthocarboxylic acid, conventionally employed in cyanine condensations, mention may be

made of triethyl orthoformate, tri-n-propyl orthoformate, triethyl orthoacetate, tri-n-propyl orthoacetate, tri!N-butyl orthoacetate, triethyl orthopropionate, tri-n-propyl orthopropionate, tri-n-butyl orthopropionate, triethyl orthobenzoate, and the like.

Employing the aforementioned orthoacetate, orthopropionate, orthobenzoate, and the like, esters, instead of orthoformate esters, provides a mechanism for producing trimethine, or carbocyanine, dye segments containing a substituent such as methyl, ethyl, phenyl, and the like, for example, at the central carbon atom, or meso, position of the trimethenyl chain.

As examples of basic condensing agents, conventionally employed in cyanine dye condensation, mention may be made of organic amines, as, for example, tri-n-propylamine, tri-n-butylamine, triisoamylamine, triethylamine, trimethylamine, dimethylaniline, diethylaniline, pyridine, N-alkyl-piperidine, and the like, and most preferably an organic tertiary amine having a dissociation constant greater than pyridine (1×10^5); an alkali metal carboxylate in a carboxylic anhydride, for example, sodium acetate in acetic anhydride, and the like; or an alkali metal hydroxide or carbonate, for example, sodium hydroxide, potassium hydroxide, potassium carbonate, and the like; with the condensation reaction effected most preferably in the presence of heat and in a substantially inert reaction medium such as a lower molecular weight alcohol, for example, ethyl, n-propyl, isopropyl, n-butyl or isobutyl alcohol, tricresyl phosphate; a phenol or cresol; or a reaction medium itself comprising the condensing agent such as pyridine.

The compounds of formula (B) may be prepared by reacting a compound of formula (C), wherein R is hydrogen, with a difunctional organic hydrocarbon compound such as an alkylene dihalide, a cycloalkylene dihalide, an alkylene ditosylate, a cycloalkylene ditosylate, an alkylene ester of alkylene and cycloalkylene disulfonic acids, an alkyl ester of an alkylene disulfonic acid, a dialkyl ester of an alkylene disulfonic acid, and the like, and mixed compounds containing the designated functional radicals, specifically, methylene dibromide; propylene dibromide; 1,2-butylene dichloride; ethylene and propylene diiodides; isobutylene dibromide; 1,1-dibromo ethane; benzylidine dichloride; omega, omega'-xylylene dibromide; omega, omega'-xylylene dichloride; cyclohexane dibromide,-1,2, -1,3 and -1,4; 1,3-dibromo-2-hydroxypropane; methane disulfonic dimethyl ester; ethane and α, β disulfonic diethyl ester; ethane α, α' disulfonic dimethyl ester; diethyl ester of ethane α, β disulfonic acid; α, β propane disulfonic diethyl ester; β-methyl propane, α, β disulfonic dimethyl ester; diethyl ester of n-hexane-, n-heptane-, and n-octane-disulfonic acid; diethyl ester of phenyl disulfonic acid; dimethyl ester of naphthalene disulfonic acid; dimethyl ester of diphenyl sulfonic acid; dimethyl α, β ethane disulfate; diethyl α, β ethane disulfate; ethylene di-(ethyl sulfonate); ethylene di(p-toluene sulfonate); ethylene di-(cyclohexyl sulfonate); p-phenylene di-(p-toluene sulfonate); propylene di(p-toluene sulfonate); hexamethylene di-(p-toluene sulfonate); and the like.

It will be apparent that the hydrocarbon radical may be substituted by various groups which do not form ternary salts, for example, nitro, primary, secondary and tertiary amino groups; hydroxyl, carbonyl, thiacarbonyl, heterocyclic, and the like.

As employed throughout the instant specification, the term "heterocyclic"ring system is intended to include both substituted and unsubstituted heterocyclic nuclei including heterocyclic ring systems which contain fused aromatic rings as a constituent component of the ring system such as benzoxazoles, benzothiazoles, benzoselenazoles, benzimidazoles, the corresponding naphthazoles and anthracenazoles and, further including, ring systems which contain substituents usual in the cyanine dye art such as lower alkyl, lower alkoxy, benzyl, phenyl, napthyl, chloro, bromo, iodo, amino, hydroxyl, and the like.

As examples of such heterocyclic nitrogen ring systems, mention may be made of those of the thiazole series e.g. thiazole, 4-methylthiazole, 5-methylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.), those of the naphthothiazole series (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 7-methoxy-α-naphthothiazole, 8-methoxy-α-naphthothiazole, etc.), those of the thianaphtheno-7',6'-4,5-thiazole series (e.g., 4'-methoxythianaphtheno-7',6'-4,5-thiazole, etc.), those of the oxazole series (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), those of the benzoxazole series (e.g., benzoxazole, 5-chlorobenzoxazole, 5-phenylbenzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-methoxybenzoxazole, 5-ethoxybenzoxazole, 6-chlorobenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.), those of the naphthoxazole series (e.g., α-naphthoxazole, β-naphthoxazole, etc.), those of the selenazole series (e.g., 4-methylselenazole, 4-phenylselenazole, etc. those of the benzoselenazole series (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.); those of the naphththoselenazole series (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.), those of the thiazoline series (e.g., thiazoline, 4-methylthiazoline, etc.), those of the 2-quiaoline series (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroquinoline, etc.), those of the 4-quinoline series (e.g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.), those of the 1-isoquinoline series (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.), those of the 3,3-dialkylindolenine series (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), those of the 2-pyridine series (e.g., pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 6-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,5-dimethylpyridine, 4,6-dimethylpyridine, 4-phenylpyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine, 4-hydroxypyridine, 5-hydroxypyridine, 6-hydroxypyridine, 3-phenylpyridine, 4-phenylpyridine, 6-phenylpyridine, etc.), those of the 4-pyridine series (e.g., 2-methylpyridine, 3-methylpyridine, 3-bromopyridine, 3-chloropyridine, 2,3-dimethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, etc.), those of the imidazole series, those of the benzimidiazole series (e.g., 5-chlorobenzimidazole, 5,6-dichlorobenzimidazole) and the like.

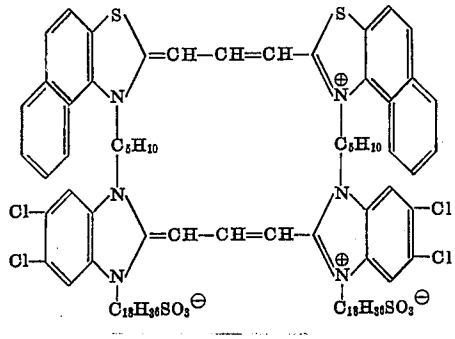
The anion, represented by the designation Y in the formulas, comprises those anionic acid radicals customary in the cyanine dye art, for example, chloride, bromide, iodide, methylsulfate, ethylsulfate, p-toluenesulfonate, benzenesulfonate, acetate, propionate, cyanate, perchlorate, and the like.

For purposes of illustrating the preceding description of the invention and in carrying out same, for example, for the

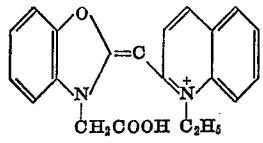
production of a photographic film element employing a photoresponsive gelatino silver halide emulsion employing optically sensitized photoresponsive silver halide crystals, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble 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 floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928, 2,614929, 2,728,662, and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, the previously detailed chemical sensitizing agents and the like; all according to the traditional procedures of etc., art, as described in Neblette, C. B., *Photography, Its Materials and Processes*, 6th Ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may then be accomplished by contact of the emulsion composition with an effective concentration, generally in the order of about 3 to 4 mgs. of a disegmented cyanine dye or about 4.5 to 6 mgs. of trisegmented cyanine dye, etc., per gram of silver. A suitable supersensitizing dye may be added in order to attain as high a quantum efficiency as the given system will permit.

For example, a suitable supersensitizer for the disegmented cyanine dye



would be



As a general rule, whether or not a given material will act as an effective supersensitizer for a particular pseudopolymeric sensitizing agent will depend upon the particular cyanine dye segment directly adsorbed to the photosensitive element and will be determined empirically by techniques well known in the photographic art.

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

Alternatively, an emulsion coating can be prepared and coated on a suitable support whereupon the coating may be sequentially immersed in a solution of the pseudopolymeric compound which is to be employed as a spectral sensitizer. In view of the foregoing exemplary material it will be appreciated that by means of the present invention an energy circuit has been established which channels photon-excitation-derived energy into a photoresponsive material by a radiationless transfer between compound segments which comprise, from the photoresponsive element, links possessing electromagnetic radiation adsorption frequency ranges in increasing order wherein the transmission ranges of each succeeding material overlaps the absorption range of the next preceding material. relatively

Within the context of the present invention it is necessary, in order to achieve optimum results, that the spectral sensitizing material adsorbed onto the photoresponsive material be present at a coverage which will produce sensitization at, or approaching, maximum for that material and the particular photoresponsive element. This area is usually reached, as aforementioned, at about or slightly less than monomolecular layer coverage. Subsequent layers of other dye materials, with appropriate adsorption and transmission frequency ranges as determined by conventional techniques, such as, for example, by wedge spectrographic means, (See *The Theory of the Photographic Process*, 3rd Ed. Mees and James, Pages 433–434) may be added over the adsorbed pseudopolymeric material as mono- or multimolecular layers, the internal quantum loss per multimolecular layer being relatively small. Critical to the proper utilization of such materials, however, is the maintenance of the energy adsorption and transmission range parameters between the terminal segment of the pseudopolymeric sensitizer directly adsorbed onto the surface of the photosensitive material and any subsequent dye layers, and further that the relationship between the subsequent dye layers one to the other be such as to provide that each succeeding dye material possess an absorption frequency range in increasing order from the surface of the photosensitive element, and a transmission frequency range within the absorption frequency range of the next preceding dye material. Ultimately then, it is evident that by continuing to add dye material to a pseudopolymerically spectrally sensitized photoresponsive element, instead of achieving the art dictated loss in sensitivity or stagnation at a given sensitivity plateau, an increase in sensitivity will be achieved with little, or substantially no degradation in the quantum efficiency of the system.

Photoresponsive crystals of the present invention may be employed as the photosensitive component of a photographic emulsion by incorporation within a suitable binder, such as gelatin 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 or silver iodobromide, of 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-butyrate, 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 azindines of U.S. Pat. Nos. 2,444,605; 2,444,606; 2,444,607; 2,450,297; 2,444,609; 2,713,541; 2,743,181; 2,716,062; 2,735,769; 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, mucochloric acid, etc., the ketone 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 a cellulose derivative, as described in U.S. Pat. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in U.S. Pat. Nos. 2,253,078; 2,276,322; 2,276,323; 2,281,703; 2,310,223; 2,311,058; 2,311,059; 2,414,208; 2,461,023; 2,484,456; 2,538,257; 2,579,016; 2,614,931; 2,624,674; 2,632,704; 2,642,420; 2,678,884; 2,691,582; 2,725,296; 2,753,264; and the like.

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 photoresponsive crystals may also be employed in the fabrication of photographic emulsions which form latent images predominantly on the surface of the crystal or in emulsions which form latent images predominantly inside the crystal such as those described in U.S. Pat. No. 2,592,250.

The fabricated emulsions may also be employed in silver diffusion transfer processes of the types set forth in U.S. Pat. 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 process 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; 3,444,873; 3,047,386; 3,065,074; 3,069,262; 3,069,262; 3,069,264; 3,076,808; 3,076,820; 3,077,400 and 3,077,402.

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 crystals, 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 the photographic emulsion and the relative 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 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 process 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.

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. Pats. Nos. 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. Pats. Nos. 2,361,019 and 2,258,423. Other types of binders which can be used in the photoconductive layers include such materials are 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. previously

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 selfsupporting 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 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 developed, 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. 2,296,691, and the like. In process of electrophotographic reproduction such as in xerography, by selecting a developing particle which has 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. Pats. Nos. 2,297,691 and 2,551,582 and "RCA Review," Vol. 15 (1954), pages 469–484.

Throughout the specification the term "photon-excitation-derived energy" is utilized. In the context of the present invention, that term describes the stimulus, induced by incident

electromagnetic radiation, which is capable of producing photochemical changes in a photosensitive material.

Since certain changes may be made in the above product and process 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 spectrally sensitized photoresponsive article comprising a photoresponsive element selected from the group consisting of photoconductors and photosensitive silver halides having a spectral sensitization system adsorbed to a surface thereof, said system comprising a compound comprising a multiplicity of segments which include, in order from the element surface, a directly adsorbed cyanine dye segment and, pendent therefrom, in chainlike configuration, at least one dye segment comprising an energy adsorbing and transmitting material, said directly adsorbed segment and subsequent segments being capable of absorbing incident electromagnetic radiation energy and photon-excitation-derived energy transmitted from at least any next distal segment of energy absorbing and transmitting material within a given frequency range and transmitting said energy within a lower frequency range, wherein said directly adsorbed segment and each more distal segment possesses an intrinsic energy absorption frequency range in increasing order outward from the photoresponsive element surface and any segment subsequent to the directly adsorbed segment possesses an intrinsic energy transmission frequency range which overlaps the energy absorption frequency range of the next preceding segment thereby establishing a circuit capable of transmitting photon-excitation-derived energy to said photoresponsive element.

2. The invention of claim 1 wherein said compound comprises from two to three segments.

3. The invention of claim 1 wherein said compound is adsorbed to said photosensitive element in a substantially monomolecular layer.

4. The invention of claim 1 wherein a material capable of supersensitizing the directly adsorbed cyanine dye segment of said chainlike compound is also adsorbed to said photosensitive element.

5. The invention of claim 1 wherein said chainlike compound comprises intersegmentary bridge bonds.

6. The invention of claim 1 wherein at least one of said segments comprises a hydrocarbon dye.

7. The invention of claim 1 wherein said chainlike compound is a linear, branched compound containing a single point of attachment between adjacent segments.

8. The invention of claim 5 wherein said segments comprise cyanine dyes.

9. The invention of claim 8 wherein said bridge bonds are accomplished through bivalent hydrocarbon groups attached to heterocyclic atoms of adjacent cyanine dye segments.

10. The invention of claim 9 wherein said bivalent hydrocarbon groups comprise alkylene groups.

11. The invention of claim 10 wherein said bivalent radicals are less than 50 A. in length.

12. The invention of claim 11 wherein said photoresponsive element comprises a silver halide crystal.

13. The invention of claim 11 wherein said photoresponsive element comprises photoconductive zinc oxide.

14. The invention of claim 12 wherein a compound capable or supersensitizing said chainlike compound is also adsorbed to said silver halide crystal and said chainlike compound and supersensitizing compound together comprise substantially a monomolecular layer on said silver halide crystal.

15. The invention of claim 14 wherein adsorbed to the terminal end of said chainlike compound most distal from said silver halide crystal is, in layered configuration, at least one compound possessing an energy absorption frequency range at a higher frequency than the energy absorption frequency range of the next proximal energy absorptive material, and an energy transmission frequency range which overlaps the energy absorption frequency range of the next proximal energy absorptive material.

16. A photoresponsive product which comprises a plurality of spectrally sensitized photoresponsive articles distributed on the surface of a support, said articles comprising photoresponsive elements selected from the group consisting of photoconductors and photosensitive silver halides having a spectral sensitization system adsorbed thereto, said system comprising a compound comprising a multiplicity of segments which include, in order from the element surface, a directly adsorbed cyanine dye segment and, pendent therefrom in chainlike configuration, at least one dye segment comprising an energy absorbing and transmitting material, said directly adsorbed segment and any subsequent segment being capable of absorbing incident electromagnetic radiation energy and photon-excitation-derived energy transmitted from at least any next distal segment of energy absorbing and transmitting material within a given frequency range and transmitting said energy within a lower frequency range, wherein said directly adsorbed segment and each more distal segment possesses an intrinsic energy absorption frequency range in increasing order outward from the photoresponsive element surface and any segment subsequent to the directly adsorbed segment possesses an intrinsic energy transmission frequency range which overlaps the energy absorption frequency range of the next preceding segment thereby establishing a circuit capable of transmitting photoniexcitation-derived energy to said photoresponsive element.

17. The invention of claim 16 wherein said plurality of photoresponsive articles is dispersed in a polymeric binder.

18. The invention of claim 17 wherein said photoresponsive elements comprise silver halide crystals.

19. The invention of claim 18 wherein said polymeric binder comprises gelatin.

20. The invention of claim 16 wherein said photoresponsive elements comprise photoconductive zinc oxide crystals.

21. The invention of claim 17 wherein said polymeric binder comprises an electrically insulating material.

22. The invention of claim 21 wherein said support comprises an electrically conducting support.

23. The invention of claim 21 including an electrically conducting layer intermediate said support and said photoresponsive article containing layer.

24. A photoresponsive product which comprises a plurality of spectrally sensitized silver halide crystals dispersed in a gelatin binder and coated on the surface of a support wherein said silver halide crystals have adsorbed thereto a substantially monomolecular layer of a spectral sensitization system comprising: a compound comprising between two and three cyanine dye segments which include, in order, from the crystal surface, a directly adsorbed segment and pendent therefrom, in chainlike configuration, from one to two additional cyanine dye segments, said cyanine dye segments being joined each to the other at one or two attachment points through divalent hydrocarbon groups wherein the intersegmentary distance is less than 50 A. each of said cyanine dye segments being capable of absorbing incident electromagnetic radiation energy and photon-excitation-derived energy transmitted from at least any next distal cyanine dye segment within a given frequency range and transmitting said energy within a lower frequency range, wherein said directly adsorbed segment and each more distal segment possesses an intrinsic energy absorption frequency range in increasing order outward from the photoresponsive element surface and any segment subsequent to the directly adsorbed segment possesses an intrinsic energy transmission frequency range which overlaps the energy absorption frequency range of the next preceding segment; and a supersensitizer for the directly adsorbed cyanine dye segment of said chainlike spectral sensitizing compound, whereby a circuit capable of transmitting photon-excitation-derived energy to said photoresponsive silver halide crystals is established.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,622,317 Dated November 23, 1971

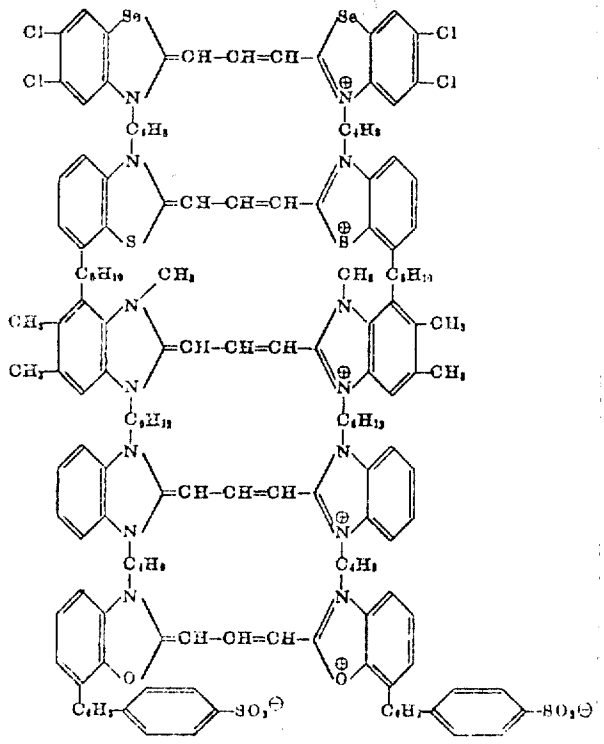
Inventor(s) George R. Bird and Alan E. Rosenoff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

REFERENCES: 8th reference, "Nltys" should be --Nhys--.

Abstract, line 4, "of spectral" should be --of a spectral--.

Column 9, in the formula which begins at line 46



should be

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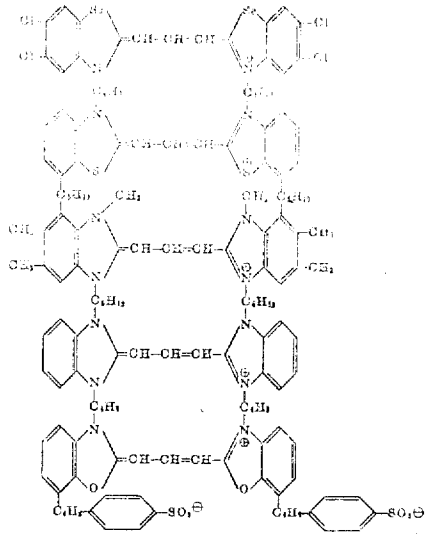
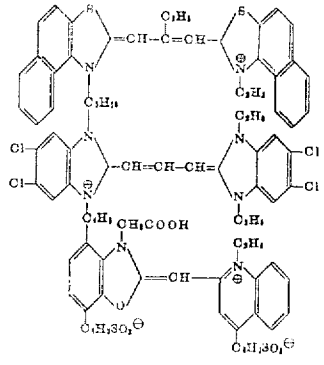
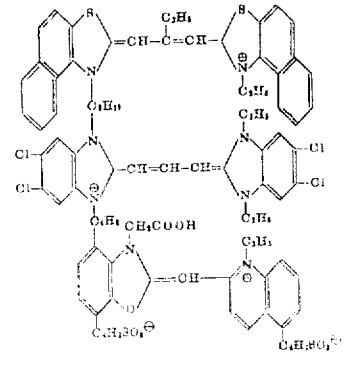


Column 11, in the formula which begins at line 20



should be



UNITED STATES PATENT OFFICE

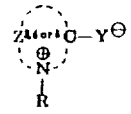
CERTIFICATE OF CORRECTION

3,622,317 PAGE - 3

Column 13, line 39 "$R^{least\ one\ of\ R,\ R^1,}$" should be --at least one of R, R^1, --.

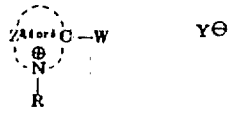
Column 14, Formula (C), line 6

(C)



should be

(C)



Column 15, line 19 "$(1X10^5)$;" should be --$(1X10^{-5})$; --.

Column 24, claim 16, line 28 "photoniexcitation-derived" should be --photon-excitation-derived--.

Signed and sealed this 18th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents