

[54] SENSITIZED PHOTSENSITIVE COMPOUNDS AND ELEMENTS 3,250,615 5/1966 Van Allen et al. 96/88

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[58] Field of Search 96/88, 90 R, 90 PC

[56] References Cited

UNITED STATES PATENTS

3,501,308 3/1970 Adelman 96/48 R

[57] ABSTRACT

The spectral sensitivity of radiation-sensitive polyyne compounds can be extended to longer wavelengths by the use of pyrylium salts, including thiapyrylium and selenapyrylium salts.

22 Claims, No Drawings

SENSITIZED PHOTOSENSITIVE COMPOUNDS AND ELEMENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

In general, this application relates to radiant-energy sensitive composition comprising radiation-sensitive crystalline polyacetylenic compounds for image-recording purposes. More particularly, this invention concerns enhancing the sensitivity of such radiant energy sensitive compositions through the utilization of particular sensitizing materials, and includes enhanced radiation-sensitive compositions and elements, and techniques for the preparation thereof.

It has been discovered that the sensitivity of polyacetylenic compounds may be substantially extended by the presence of pyrylium, thiapyrylium, and selenapyrylium compounds. Thus, high speed print-out elements may be prepared having enhanced sensitivity to radiation in the visible region.

2. Description of the Prior Art

Numerous polyacetylenic compositions of matter are reported in the literature along with observations that some undergo color change upon exposure to light and/or ultraviolet radiation. Included among investigators reporting on polyyne compositions are: Arthur Seher; Ferdinand Bohlmann and his coauthors; and E. R. H. Jones and M. C. Whiting and their coauthors. The radiation-sensitive polyacetylenic compounds taught in the art typically contain a minimum of two acetylenic linkages as a conjugated system (i.e., $-C \equiv C - C \equiv C -$) and, with only a few exceptions, carbon atoms in alpha positions to the acetylenic carbon atoms, i.e., those carbon atoms directly connecting to the acetylenic carbon atoms are bonded directly only to carbon and/or hydrogen atoms. The radiation-sensitive polyacetylenic compositions of matter encompass diynes, triynes, tetraynes, higher polyyenes and numerous derivatives and related compounds thereof of various chemical classes ranging from hydrocarbon compounds to acids, esters, and diols, to still other compounds of other chemical classifications containing numerous and varied organic radicals stemming from the conjugate acetylenic carbon atoms.

As is apparent from publications of the aforementioned investigators, methods are known in the art for the preparation of polyacetylenic compositions. Methods also are taught in U.S. Pat. Nos. 2,816,149; 2,941,014; 3,065,283; etc. General preparative methods include: oxidative coupling or oxidative dehydrocondensation reactions of numerous terminal acetylenic compounds to prepare as desired, symmetrical and unsymmetrical polyyne compounds; dehydrohalogenation reactions to provide compounds containing acetylenic bonds; and variations, modifications, and combinations of such basic reactions to provide preparative routes for a multitude of polyacetylenic compositions of matter.

From the preceding description of the art and the sources therein mentioned, there are apparent numerous polyyne compounds which may be suitable for use in this invention. For some there is a brief mention of radiation sensitivity, generally in the ultraviolet range, while for others nothing is reported as to radiation sensitivity. However, it is within the skill of the art to readily evaluate a polyyne's sensitivity to any given radiation where the same is unknown. Thus, one needs

merely to expose samples of a prepared crystalline polyacetylenic composition of matter to various forms of radiant energy and upon exposure to observe whether a visible color change occurs in the exposed composition. If a visible color change occurs upon exposure to a form of radiant energy, then the crystalline polyacetylenic compositions of matter is deemed sensitive, for purposes of the present invention, to that specific form of radiant energy.

Radiant energy, as used herein, is intended to include numerous variant forms of radiant energy, encompassing not only the ultraviolet and visible regions (i.e., actinic radiation) and infrared region of the electromagnetic spectrum, but also electron beams, such as developed by cathode ray guns, gamma-rays, x-rays, beta-rays, electrical corona discharge, and other forms of corpuscular and/or wave-like energy generally deemed to be radiant energy. The various individual crystalline polyacetylenic compositions of concern generally are not responsive to all such forms of radiant energy, but selectively respond to at least one or more of several variant forms thereof. Within the numerous and varied useful crystalline polyacetylenic compositions of matter, some respond rapidly and selectively to certain radiant energy forms, and slowly or not at all to other forms of radiant energy. Most frequently, response to a particular form of radiant energy is greatest, and most rapid, at particular narrow regions and wavelengths of the electromagnetic spectrum. Generally, the preferred polyacetylenic compositions are most sensitive to radiation within the ultraviolet region.

Depending on particular requirements for a desired application, such as temperature of use, radiant energy form employed, desired speed of response, desired color of image, and the like, there is presently available a wide selection of useful radiation-sensitive crystalline polyacetylenic compositions of matter for use in image-recording applications. However, as previously noted, polyacetylenic compositions have in the past been highly sensitive to ultraviolet radiation, and less sensitive to radiation of longer wavelengths. Although some of the polyyenes comprising the materials described in the prior art are inherently sensitive to visible radiation, their degree of sensitivity is usually low and in the short wavelength portion of the spectrum, so that it is desirable to add materials to increase their sensitivity and to shift the sensitivity toward the longer wavelength portion of the spectrum. Increasing the sensitivity of such systems in the visible regions of the spectrum has several advantages: it makes available inexpensive and convenient light sources, such as incandescent lamps; it reduces exposure time; and it allows projection printing through various optical systems.

It is, therefore, an object of our invention to provide a novel class of sensitizers for radiation-sensitive systems which produces an unusual increase in sensitivity and extends the range of sensitivity into the longer wavelengths of the visible spectrum.

Another object is to provide a novel class of sensitizers for crystalline polyacetylenic compositions.

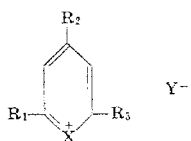
It is another object to provide useful sensitized compositions comprising a radiation-sensitive crystalline polyacetylenic compound and a pyrylium, thiapyrylium, or selenapyrylium sensitizer.

A further object is to provide processes for the preparation of the sensitized compositions, for employment of the same in image-recording applications, and for

processing exposed sensitized compositions in various applications.

SUMMARY OF THE INVENTION

These and other objects are obtained by the practice of this invention, which invention resides in the use of radiation-sensitive film forming compositions comprising a polyacetylenic compound and a pyrylium compound represented advantageously by the following formula:



wherein R_1 , R_2 and R_3 may each represent an aliphatic group having from 1 to 15 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl, isoamyl, hexyl, octyl, nonyl, dodecyl, vinyl, styryl, alkoxystryl, diethoxystyryl, dimethylaminostyryl, 1-butyl-4-p-diethylaminophenyl-1,3-butadienyl, β -ethyl-4-dimethylaminostyryl; an alkoxy group such as methoxy, ethoxy, propoxy, butoxy, amyloxy, hexoxy, octoxy, etc.; aryl, such as phenyl, 4-biphenyl, alkylphenyl, such as 4-ethylphenyl, 4-propylphenyl, etc., alkoxyphenyl, e.g., 4-ethoxyphenyl, 4-methoxyphenyl, 4-amyloxyphenyl, 2-hexoxyphenyl, 2-methoxyphenyl, 2-amyloxyphenyl, 3,4-dimethoxyphenyl, etc.; ω -hydroxy alkoxyphenyl, e.g., 2-hydroxyethoxyphenyl, 3-hydroxyethoxyphenyl, etc., 4-hydroxyphenyl, halophenyl, e.g., 3,4-dichlorophenyl, 3,4-dibromophenyl, 4-chlorophenyl, 2,4-dichlorophenyl, etc. azidophenyl, nitrophenyl, etc., aminophenyl, e.g., 4-diethylaminophenyl, 4-dimethylaminophenyl, etc.; X is oxygen, sulfur or selenium (preferably oxygen or sulfur); and Y is an anionic function.

Typical members of the suitable pyrylium salts include the following:

Compound Number	Name of Compound
1	2,4,6-Triphenylpyrylium perchlorate.
2	4-(4-Methoxyphenyl)-2,6-diphenylpyrylium perchlorate.
3	4-(2,4-Dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
4	4-(3,4-Dichlorophenyl)-2,6-diphenylpyrylium perchlorate.
5	2,6-Bis(4-methoxyphenyl)-4-phenylpyrylium perchlorate.
6	6-(4-Methoxyphenyl)-2,4-diphenylpyrylium perchlorate.
7	2-(3,4-Dichlorophenyl)-4-(4-methoxyphenyl)-6-phenylpyrylium perchlorate.
8	4-(4-Amyloxyphenyl)-2,6-bis(4-ethylphenyl)pyrylium perchlorate.
9	4-(4-Amyloxyphenyl)-2,6-bis(4-methoxyphenyl)pyrylium perchlorate.
10	2,4,6-Triphenylpyrylium fluoborate.
11	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium perchlorate.
12	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)pyrylium fluoborate.
13	6-(3,4-Diethoxystyryl)-2,4-diphenylpyrylium perchlorate.
14	6-(3,4-Diethoxy- β -amylstyryl)-2,4-diphenylpyrylium fluoborate.
15	6-(4-Dimethylamino- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
16	6-(1-n-Amyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
17	6-(4-Dimethylaminostyryl)-2,4-diphenylpyrylium fluoborate.
18	6-(α -Ethyl- β , β -dimethylaminophenyl vinylene)-2,4-diphenylpyrylium

19	fluoroborate.
20	6-(1-Butyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
21	6-(4-Dimethylaminostyryl)-2,4-diphenylpyrylium perchlorate.
22	6-[β , β -Bis(4-dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium perchlorate.
23	2,6-Bis(4-dimethylaminostyryl)-4-phenylpyrylium perchlorate.
24	6-(β -Methyl-4-dimethylaminostyryl)-2,4-diphenylpyrylium fluoborate.
25	6-(1-Ethyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
26	6-[β , β -Bis(4-dimethylaminophenyl)vinylene]-2,4-diphenylpyrylium fluoborate.
27	6-(1-Methyl-4-p-dimethylaminophenyl-1,3-butadienyl)-2,4-diphenylpyrylium fluoborate.
28	4-(4-Dimethylaminophenyl)-2,6-diphenylpyrylium perchlorate.
29	2,6-Bis(4-ethylphenyl)-4-phenylpyrylium perchlorate.
30	2,6-Bis(4-ethylphenyl)-4-methoxyphenylthiapyrylium fluoborate.
31	2,4,6-triphenylthiapyrylium perchlorate.
32	4-(4-Methoxyphenyl)-2,6-diphenylthiapyrylium perchlorate.
33	6-(4-Methoxyphenyl)-2,4-diphenylthiapyrylium perchlorate.
34	2,6-Bis(4-methoxyphenyl)-4-phenylthiapyrylium perchlorate.
35	4-(2,4-Dichlorophenyl)-2,6-diphenylthiapyrylium perchlorate.
36	2,4,6-Tri(4-methoxyphenyl)thiapyrylium perchlorate.
37	2,6-Bis(4-ethylphenyl)-4-phenylthiapyrylium perchlorate.
38	4-(4-Amyloxyphenyl)-2,6-bis(4-ethylphenyl)thiapyrylium perchlorate.
39	6-(4-Dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
40	2,4,6-Triphenylthiapyrylium fluoborate.
41	2,4,6-Triphenylthiapyrylium sulfate.
42	4-(4-Methoxyphenyl)-2,6-diphenylthiapyrylium fluoborate.
43	2,4,6-Triphenylthiapyrylium chloride.
44	2-(4-Amyloxyphenyl)-4,6-diphenylthiapyrylium fluoborate.
45	4-(4-Amyloxyphenyl)-2,6-bis(4-methoxyphenyl)thiapyrylium perchlorate.
46	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
47	4-Anisyl-2,6-bis(4-n-amyloxyphenyl)thiapyrylium chloride.
48	2-[β , β -Bis(4-dimethylaminophenyl)vinylene]-4,6-diphenylthiapyrylium perchlorate.
49	6-(β -Ethyl-4-dimethylaminostyryl)-2,4-diphenylthiapyrylium perchlorate.
50	2-(3,4-Diethoxystyryl)-4,6-diphenylthiapyrylium perchlorate.
51	2,4,6-Triphenylthiapyrylium perchlorate.
52	6-Ethyl-2,4-diphenylpyrylium fluoborate.
53	2,6-Bis(4-ethylphenyl)-4-(4-methoxyphenyl)thiapyrylium chloride.
54	6-[β , β -Bis(4-dimethylaminophenyl)vinylene]-2,4-di(4-ethylphenyl)pyrylium perchlorate.
55	2,6-Bis(4-amyloxyphenyl)-4-(4-methoxyphenyl)thiapyrylium perchlorate.
56	6-(3,4-Diethoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
57	6-(4-Methoxy- β -ethylstyryl)-2,4-diphenylpyrylium fluoborate.
58	2-(4-ethylphenyl)-4,6-diphenylthiapyrylium perchlorate.
59	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium perchlorate.
60	2,6-diphenyl-4-(4-methoxyphenyl)thiapyrylium fluoborate.
61	2,6-bis(4-ethylphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate.
62	2,6-bis(4-methoxyphenyl)-4-(4-n-amyloxyphenyl)thiapyrylium perchlorate.
63	2,4,6-tri(4-methoxyphenyl)thiapyrylium fluoborate.
64	2,4-diphenyl-6(3,4-diethoxystyryl)pyrylium perchlorate.
65	2,4,6-Triphenylselenapyrylium perchlorate.
66	4-(n-butylamino)-2-(4-methoxyphenyl)benzo [b] pyrylium perchlorate.
	4-(n-butylamino)-2-phenylbenzo [b]

In general, pyrylium salts have been found to be useful sensitizers for polyacetylenic compounds. However, it should be noted that each compound does not necessarily provide the same enhancement of sensitivity. This is particularly true in regards to different classifications or classes of polyacetylenic compounds. For example, whereas certain pyrylium dyes may provide relatively little enhancement of the radiation-sensitivity of an alkali metal salt of a polyacetylenic dioic acid, the same dye may provide a large enhancement of the radiation-sensitivity of an alkyl amide derivative of a polyacetylenic polyoic acid. Similarly, other pyrylium salts may have little effect upon alkyl amide derivatives of polyacetylenic compounds, but may greatly enhance the sensitivity of polyacetylenic amine salts, or urethane derivatives of diyne diols.

Enhancement provided by the pyrylium salt as a sensitizer for the polyne compound is evidenced by the sensitized composition being able to undergo a significant color change upon exposure to a wavelength of radiant energy other than that to which it was principally sensitive in its unsensitized form. Usually the enhancement manifests itself by the sensitized composition being sensitive at a longer wavelength. For example, a polyne compound particularly sensitive to ultraviolet radiation of 2537 Å. wavelength may possess little or no significant sensitivity to normal daylight. After comingling such a polyne compound with a pyrylium salt, the resultant sensitized crystalline composition possesses a significant sensitivity to normal daylight. Often this providing of significant daylight photosensitivity is accompanied by little or no appreciable loss of the polyne's initial ultraviolet sensitivity. The enhancement provided by the pyrylium compound is accompanied by a deeper color change and/or faster speed of response of the sensitized composition to the radiant energy inducing the color change.

The sensitized compositions of this invention are prepared by comingling with each other a radiation-sensitive crystalline polyacetylenic compound, and a pyrylium compound such as previously described. This comingling should provide intimate contact between at least some of the employed polyacetylenic compound and the pyrylium salt sensitizer.

A number of suitable polyacetylenic compositions of matter for utilization in the process and elements of this invention are disclosed in U.S. Pat. No. 3,501,302. The polyacetylenic compositions described therein include radiation-sensitive crystalline acid derivatives, and in particular, certain esters and salts of dicarboxylic-terminated polyacetylenic compounds having the structural formula $\text{HOOC}-(\text{CH}_2)_m-(\text{C}\equiv\text{C})_n-(\text{CH}_2)_m-\text{COOH}$, wherein n is an integer of at least 2 and m^1 and m^2 are integers, not necessarily the same but preferably the same, greater than 5 and less than 10. The preferred photosensitive crystalline acid derivatives disclosed by said patents include: the mono- and diesters of these diacids, and especially of the symmetrical diacetylenic diacids, with particular preference for the lower alkyl esters, and most specifically the alkyl ester derivatives wherein the alkyl-ester moiety contains less than 3 carbon atoms; and alkali metal salts and acid derivatives of these diacids and their half-esters of the preferred symmetrical diacetylenic diacids. Particularly preferred is the monomethyl ester of 10,12-docosadiynedioic acid.

Further polyacetylenic compositions which are suitable for utilization according to this invention include alkylamide derivatives such as those which have the structural formula $\text{A}-(\text{CH}_2)_x-(\text{C}\equiv\text{C})_n-(\text{CH}_2)_y-\text{B}$, wherein: n is an integer greater than 1; x and y are each an integer from 0 to 10; A may be a methyl radical, either unsubstituted or substituted, (such as methoxymethyl or ethoxymethyl), COOR, CONHR', CONHNHR'' or CONHCONHR'', and B is a radical selected from the group consisting of CONHR', CONHNHR'', and CONHCONHR'', wherein R may be H or an alkyl of 8 or less carbon atoms (e.g., methyl, propyl, pentyl, octyl, etc.), R' is an alkyl having from 2 to 12 carbon atoms, (e.g., propyl, butyl, octyl, decyl, undecyl, etc.), including substituted alkyls such as hydroxy, polyhydroxy, amino, substituted amino, alkyl thio, COOR, CONHR', or methoxy substituted alkyl, and R'' may be phenyl or an alkyl having from 2 to 12 carbon atoms. Preferred alkylamides of this nature include: methyl 21-[N-(3-carboxypropyl)carbamoyl]-10,12-heneicosadiyne; methyl 21-[N-(3-hydroxypropyl)carbamoyl]-10,12-heneicosadiynoate; and methyl 21[N-3-carboxypropyl]carbamoyl]-10,12-heneicosadiynoate.

Suitable radiation-sensitive crystalline polyacetylenic amine salts may have the structural formula $\text{B}-\text{CH}_2-\text{C}\equiv\text{C}-(\text{CH}_2)_n-\text{CH}_2-\text{COO}^-\text{A}^+$, wherein: n is an integer greater than 1; x and y are each an integer from 0 to 10; A^+ is selected from ammonium and substituted ammonium groups, (e.g., $\text{N}^+\text{H}_3\text{R}$, $\text{N}^+\text{H}_2\text{RR}^1$, $\text{N}^+\text{HRR}^1\text{R}^2$, $\text{N}^+\text{RR}^1\text{R}^2\text{R}^3$); B is selected from the group consisting of CH_3 , COO^-A^+ , COOR⁴, CONHR⁵, CONHNHR⁶, CONHCONHR⁶, R⁷OOCNH, and R⁷NHCOO radicals, wherein R, R¹, R², and R³ may be the same or different, and may be H, alkyl (including hydroxy or methoxy substituted alkyl), or aryl, R⁴ may be H or an alkyl of 8 or less carbon atoms (e.g., methyl, propyl, pentyl, octyl, etc.), R⁵ is an alkyl of from 2 to 12 carbon atoms (e.g., propyl, butyl, octyl, decyl, undecyl, etc.), including substituted alkyl such as hydroxy, polyhydroxy, amino, substituted amino, alkyl thio, carboxy, or methoxy substituted alkyl, R⁶ may be phenyl or an alkyl having from 2 to 12 carbon atoms, and R⁷ is an alkyl, including methoxy or hydroxy substituted alkyls of from 1 to 8 carbon atoms, phenyl, or hydroxy substituted phenyl. Suitable polyacetylenic amine salts include hexylammonium 20-(N-hexylcarbamoyl)-9,11-eicosadiyne-1-carboxylate, propylammonium 20-(N-propylcarbamoyl)-9,11-eicosadiyne-1-carboxylate, and 3-hydroxy-propylammonium 20-N-(3-hydroxypropyl)carbamoyl)-9,11-eicosadiyne-1-carboxylate.

Additional suitable polyacetylenic compounds include polyacetylenic bis urethanes corresponding to the formula $[\text{R}-\text{NHCOO}(\text{CH}_2)_n\text{C}\equiv\text{C}]_2$ wherein n is an integer of 1 to 4, and R is selected from the group consisting of alkyl radicals of from 1 to 12 carbon atoms, including substituted alkyl radicals such as hydroxy, polyhydroxy, amino, substituted amino, or methoxy substituted alkyl, phenyl and substituted phenyl radicals (e.g., hydroxy, carboxy, and methoxy phenyl). Suitable members of this class of polyacetylenic compounds include 2,4-hexadiyne-1,6-diol bis (N-hexylurethane), and 2,4-hexadiyne-1,6-diol bis (N-butylurethane).

In the practice of the invention there is employed an image-receptive element comprising a carrier means

which serves to fixedly position crystals of the radiation-sensitive crystalline polyacetylenic composition. The carrier means functions to hold individual crystals in fixed position in relation to other crystals so that the element, unexposed and exposed, can be handled and moved without displacement and change in position of crystals with respect to each other.

The carrier means can be in any of several diverse embodiments. Generally, the carrier means comprise a binder material, such as a natural or synthetic plastic, resin, colloid or gel and the like, wherein the crystals of the photosensitive crystalline polyacetylenic composition of matter are dispersed and held in fixed position. In such instances, the polyene composition may be mixed as a dope, solution, emulsion, dispersion or the like with the binder material and then processed to provide solid films, sheets, coatings, and the like containing dispersed crystals of the sensitive polyacetylenic composition. Thus, one embodiment of the image-receptive element is a solid sheet, film, or the like, comprising a binder material as a dispersing medium to position fixedly therein crystals of the radiation-sensitive polyacetylenic composition. Another embodiment of the element is a support material or body to which adheres a film, coating, or the like of the binder material having the dispersed crystals therein. Useful support materials include paper sheet, glass sheet, plastic film, and other conventional and suitable photographic quality support materials. Still an additional embodiment of the element may comprise the support material having adhered thereto a binder-free coating of the crystals of the sensitive polyacetylenic composition of matter. Other element embodiments, as desired, may include a suitable photographic coating material on one or more surfaces and interfaces of the various element embodiments. In addition, other embodiments may comprise polyene crystals and support means of any of various combinations of the several foregoing components and still other components apparent to those in the art, so long as the carrier means fixedly positions the radiation-sensitive crystalline polyacetylenic composition.

Exemplary support materials include: vitreous materials, such as glass, glazed ceramics, porcelain, etc.; fibrous materials, such as cardboard, fiberboard, paper including bond paper, resin and clay-sized papers, wax or other transparentized paper, paperboard, etc.; cloths and fabrics including those of silk, cotton, viscose rayon, etc.; metals, such as copper, bronze, aluminum, tin, etc.; natural polymers and colloids, such as gelatin and polysaccharides; natural and synthetic waxes, including paraffin, beeswax, carnauba wax, synthetic resins and plastics, including particularly polyethylene, polypropylene, polymers and copolymers of vinylidene and vinylmonomers including polyvinyl chloride, polyvinylidene chloride, vinyl chloride/vinyl acetate, vinyl acetate/acrylate, vinyl acetate/methacrylate, vinylidene chloride/acrylonitrile, vinylidene chloride/vinyl acetate, vinylidene chloride/methacrylate, polystyrenes, polyvinyl acetals including polyvinyl butyral, polyvinyl formal, polyvinyl alcohol, polyamides including polyhexamethylene adipamides, N-methoxymethyl polyhexamethylene adipamide, natural and synthetic rubbers including butadiene-acrylonitrile copolymers, 2-chloro-1,3-butadiene polymers, polyacrylate polymers and copolymers including polymethylmethacrylate, polyethylmethacrylate, polyurethanes, polycarbonates, polyethylene terephthalate, polyethylene

terephthalate/isophthalate copolymers and other esters, such as obtained by condensing terephthalic acid and its derivatives with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane-1,4-dimethanol, cellulose ethers including methyl cellulose, ethyl cellulose and benzyl cellulose, cellulose esters and mixed esters including cellulose acetate, triacetate, cellulose propionate, cellulose nitrate and cellulose diacetate; and even nonthermoplastic materials including cellulose, phenolic resins, melamine-formaldehyde resins, alkyd resins, thermosetting acrylic resins, epoxy resins, and numerous other synthetic resins, and plastics as will be apparent to those skilled in the art.

The base or support material may be transparent, translucent, or opaque, and should be selected with due consideration being driven to the particular radiant energy to which the employed crystalline polyacetylenic compound is sensitive. It is also selected with due consideration of the intended usage of the imaged element and of the specific radiant energy and technique to be employed in the particular image-recording application. For example, where the imaging technique requires transmission of a specific radiation through the support to expose the polyacetylenic crystals, the support should possess such a transmission characteristic. The base or support may be adhered directly to the radiation-sensitive crystals, or indirectly adhered, if desired, by a subbing layer or coating for any of several purposes, e.g., to alter the support's transmission of the radiant energy, to change the support's reflectivity of the radiant energy, to modify adherence to the support or for other reasons. Similar to the support material, such subbing layer is selected with due regard to the specific radiant energy and technique to be employed in the particular image-recording application. Subbing layers for various photographic purposes and methods of coating supports with the same are well known.

Generally, and preferably, the element is a flat film, sheet, plate or the like, so as to present a flat surface upon which the radiant energy may be directed. However, curved-surfaced and other than flat-surfaced elements, although generally of lesser utility, are not excluded.

Exemplary binder materials of utility as components for the carrier means include: natural and synthetic plastic resins, waxes, colloids, gels and the like including gelatins, desirably photographic-grade gelatin, various polysaccharides including dextran, dextrin, hydrophylic cellulose ethers and esters, acetylated starches, natural and synthetic waxes including paraffin, beeswax, polyvinylacetals, polymers of acrylic and methacrylic esters and amines, hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic esters and styrene, vinyl acetate polymers and copolymers and their derivatives, including completely and partially hydrolyzed products thereof, polyvinyl acetate, polyvinyl alcohol, polyethylene oxide polymers, polyvinylpyrrolidone, polyvinyl acetals including polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl sodium-o-sulfobenzaldehyde acetal, polyvinyl formaldehyde acetal, and numerous other known photographic binder materials including a substantial number of aforelisted useful plastic and resinous support materials which are capable of being placed in the form of a dope, solution, dispersion, gel, or the like for incorporation therein of the radiation-

sensitive polyacetylenic composition and are then capable of processing to a solid form containing dispersed crystals of the polyacetylenic composition. As is well known in the art, in the preparation of smooth uniform continuous coatings of binder materials, there may be employed therewith small amounts of conventional coating aids as viscosity controlling agents, leveling agents, dispersing agents, and the like. The particular binder material employed is selected with due regard to the specific radiant energy and technique to be employed in the particular image-recording application and invariably is a binder material permitting substantial transmission of that specific radiant energy to be employed. Desirably, the binder material is a nonsolvent, or possesses only limited solvating properties for the polyne so that the polyne is capable of existence in its radiation-sensitive crystalline form therein.

Well-known sources, lenses and optical systems, camera arrangements, focusing and projection systems and the like for the various forms of radiant energy are used in employing the image-receptive element in the varied image-forming application, such as specimen photography, pattern making, reproduction of written, printed, drawn, typed, and the like matter and the recording of line graphical images by an impinging pointed beam of the radiant energy on the element with either or both the element and pointed beam guided or traveling to trace the image. The resultant images are directly formed printout images in that they can be seen by the human eye to be a distinctly different color than unirradiated crystals of the element, and require no chemical treatment or processing to attain visibility.

The image-receptive element may be used in image-forming systems based on transmission-exposure techniques and reflex-exposure techniques. Thus, stencils of a material substantially nontransmissive of the radiant energy may be laid on the image-forming element with the cut-out portion of the stencil allowing the applied radiant energy to strike the element according to the desired image or images. If desired, the stencil need not contact the element, with the radiant energy being projected to pass through the cut-out portion of the stencil to strike the element. The element also can be exposed by contact or projection techniques through a two-tone image or process transparency, e.g., a process negative or positive (i.e., an image-bearing transparency consisting of areas transmissive and opaque to the radiant energy, such as a so-called line or halftone negative or positive-type transparency) or a continuous tone negative or positive. Likewise, an object whose image is to be obtained may be placed between the radiant energy source and the element, and the radiant energy striking the element will be of an image pattern dependent on the radiant energy absorption and transmission characteristics of the particular object. Reflex exposure techniques are applicable. For example, by ultraviolet reflecting optic techniques, ultraviolet sensitive image-receptive elements may be used to make photocopies of printed or typed copy. Reflex-exposure techniques are particularly useful for making office copies from materials having messages on both sides of a page, for making images of specimens and objects, and for reproducing messages and the like found on materials not having radiant energy transmissive properties conducive to transmission-exposure techniques.

Where the imaged elements are to be retained for lengthy periods, desirably they are stored, as in an en-

velope or opaque container, in a manner excluding any stray irradiation of radiant energy of a form affecting the element. This may also be effectively accomplished by overcoating the imaged element with a layer of material which absorbs radiation to which the element is sensitive. Thus, an ultraviolet absorbing layer may be coated over the imaged element. Alternatively, the initially imaged elements may be fixed or converted to a more stable imaged state. In fixing, the unexposed crystalline polyne is placed in a form in which it is no longer substantially radiation-sensitive, as by solvating it in the binder, changing it from crystalline to liquid state, or washing it out from the element, and the like. In conversion, the initial irradiation induced color is often transformed to another distinctly different color, which is relatively stable to exposure to the initial form of radiant energy inducing the image formation.

A particularly convenient manner to effect a color transformation of the initially induced image is to carefully heat the imaged element to an appropriate elevated temperature, generally between 5°-20°C less than the melting point of the nonirradiated crystalline polyne, at which temperature the initial radiant-energy induced color-transformed crystals and crystal portions transform to a distinctly different color. Temperatures approximating and higher than the melting point of the unirradiated crystalline polyne will effect a color transformation of the initial radiant-energy induced colored polyne crystals, but in so doing there may be some loss in sharpness of the image with some blurring and roughing of the image border or periphery. This can be avoided, or at least minimized, if the colored crystal portions and crystals are firmly held at these temperatures so as to avoid being overcoated or dissolved in melted unexposed polyne.

Another manner for effecting color transformation of the initial color image is exposure to a solvent for the unexposed polyne. An exposure for about 10 to 15 seconds at an elevated temperature from about 5° to 10° lower than employable for heat fixing generally is satisfactory. Methanol, ethanol, toluene, diethyl ether, butyl acetate, carbon tetrachloride, acetone, 2-butoxyethanol, and like solvents are useful. Water vapor and aqueous solutions, such as aqueous hydrochloric acid, are useful with water soluble polyne derivatives. Other useful solvents also will be apparent.

An advantage of the element having the image thereof in a distinctly different color than the initial radiation-induced color, is that this other color may be more susceptible to providing print-out copies with good contrast when prints, negatives, and the like, of this image are made by conventional silver halide photographic techniques.

As indicated above, image recording elements utilizing radiation sensitive polyynes may be prepared by fixing the crystalline polyne on a surface. This may be done, for example, by coating a dispersion of the polyne in a polymer matrix on a suitable support, by coating a solution of the polyne in a polymer solution and allowing the polyne to crystallize upon solvent evaporation, by applying a solution of a polyne to a paper surface and allowing the polyne to crystallize upon the fibers, by coating a dispersion of a water immiscible polyne solution in an aqueous binder and allowing evaporation to form polyne crystals in the binder matrix, or by simply smearing the polyne crystals on a suitable support.

A particularly advantageous technique for preparing radiation-sensitive elements according to this invention is by the dissolution of radiation-sensitive polyyne crystals in one or more substantially water-immiscible organic solvents (i.e., about 0–25 percent soluble in water, by weight) which are then added to an aqueous solution of a hydrophilic binder. The water-immiscible polyyne solution is then dispersed in the aqueous binder solution, which may also contain a suitable surfactant, and mechanically stirred such as by means of a homogenizer or ultrasonic agitator, to form an "oil-in-water" dispersion, substantially devoid of polyyne crystals. This dispersion is then coated on a suitable support, during which coating the water-immiscible solvent evaporates from the coating with concomitant production of extremely fine crystals of the polyyne, uniformly distributed in the coated hydrophilic carrier. The polyyne elements thus formed are highly sensitive to various forms of radiation, are extremely uniform in particle size, and are very stable. It is desirable that the organic solvent employed to dissolve the polyacetylenic compound according to this technique be water-immiscible, or essentially so. Thus, solvents having solubilities in water of from 0 percent to about 25 percent are suitable. Exemplary organic solvents include cyclohexanone, ethyl acetate, cyclohexane, dichloromethane, dichloroethane, chloroform, pentyl alcohol, hexyl alcohol, 4-methyl-2-pentanone, benzene, toluene and the like, and mixtures thereof. Varying amounts of solvent may be employed, but generally, from 1 to 5 units (by weight) of solvent may be employed for each unit of polyacetylene to be used, with from 2 to 3 times as much solvent as polyyne being the preferred range. If water-miscible solvents are employed, an immediate precipitation of dissolved polyyne occurs upon mixing of solvent and aqueous binder solutions, resulting in relatively large average grain size, and accordingly, lower stability and control.

The time required for complete dispersion may vary from several seconds to several hours, dependent upon dispersal technique, materials employed, and size of dispersed phase droplets desired. In general, crystals averaging 1 micron in cross section, may be obtained from an emulsion formed by ultrasonically dispersing a polyyne solution in an aqueous binder for 1 to 2 minutes. It is to be recognized, however, that blending time may be so selected as to achieve the desired results in accordance with the specific materials employed.

Varying amounts of the polyyne and/or binder material may be chosen, dependent upon anticipated use of the elements produced, among other factors. In general, polyyne to binder ratios (by weight) may range from about 0.1 to about 3.0 or higher. In terms of coating density, sufficient polyyne may be utilized to provide from about 10 to 2,000 mg of polyyne per square foot of coated element. As indicated, the amount of polyyne employed is quite widely variable, and may be varied to suit the desired utilization, binder, and solvent employed. It is also possible to employ a plurality of crystalline polyacetylenic compounds.

In preparing the sensitized elements of this invention, the sensitizing material may be separately dispersed in the solvent employed to dissolve the polyacetylenic compound, and added to the aqueous binder solution with the polyacetylenic solution. Alternatively, the sensitizer may be separately dispersed in the aqueous binder solution.

The amount of sensitizer which can be added to a particular composition to give optimum sensitization can vary widely. The optimum amount will, of course, vary with the polyyne employed as well as with the particular sensitizing compound. In general, substantial gains can be obtained where an appropriate sensitizer is added at a concentration in a range of from about 0.1 percent to about 50 percent by weight, based on the weight of the polyyne, and preferably about 2.5 percent to about 5 percent, by weight, although more or less of the sensitizer may be employed if desired.

After blending according to the above described dispersal technique, the polyacetylenic compound is present in the aqueous binder solution in the form of finely divided, discrete globules of dissolved polyacetylene, which are essentially insoluble in the continuous phase. The emulsion is generally quite stable, and may, in some cases, be stored for considerable lengths of time before utilization without settling, agglomeration, or breaking, dependent upon the specific polyyne, solvent, and concentrations of each employed.

Radiation-sensitive elements may be prepared by coating the thus formed emulsion upon a suitable support and evaporating the dispersed solvent phase. Any suitable coating means may be employed, such as dip coating, air knife coating, curtain coating, flow coating, bar coating, etc. The coating may be chill set, for ease of handling, if so desired, or allowed to dry to a solid continuous phase at room temperature. During the drying stage, the organic solvent volatilizes, causing the precipitation of discrete particules of radiation-sensitive crystalline polyacetylenic compound.

In addition to comingling in a solvent and subsequent crystal formation, other suitable sensitization techniques include fusion of the sensitizer with the polyyne; absorption of the sensitizer to the surface of the polyyne; and presence of the sensitizer in the matrix surrounding the polyyne crystals.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention is further illustrated by the following examples.

Example 1

A solution of 2,4,6-triphenylpyrylium fluoborate in acetone (0.333 grams/liter) is prepared. To 0.1 ml of this solution is added 0.1 ml of an acetone solution containing 30 grams/liter of the monomethyl ester of 10,12-docosadiynedioic acid. A control solution containing 15 grams/liter of the diyne in acetone is also prepared. Drops of the test solution and the control solution are placed on a sheet of filter paper and allowed to dry in the dark. The dried spots are exposed for 75 seconds to the output from a 210 watt high pressure mercury arc; the radiation is filtered through 5 cm of water, a 4047 Å interference filter, and two CSO-52 Corning filters. The intensity of the essentially monochromatic 4047 Å radiation thus obtained is 1.1×10^{15} quanta/sec/cm², and the total exposure of the spots is 8.2×10^{16} quanta/cm². After exposure, the test spot has a distinct blue coloration; the control spot shows no coloration. The filter paper is washed with acetone to remove the unreacted diyne and the dye. In the process the blue photoproduct is converted to a red form. The intensity of the red spot is approximately the same as that of the original blue spot. A test spot prepared in

the dark, utilizing the sensitized solution, shows a visible blue coloration after a two minute exposure to the ambient fluorescent light in the laboratory.

Example 2

An acetone solution containing the monomethyl ester of 10,12-docosadiynedioic acid (15 grams/liter) and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate (0.15 grams/liter) is prepared. A control solution contains 15 grams/liter of the diyne in acetone. Drops of the test solution and of the control solution not containing the thiapyrylium dye are placed on a filter paper and allowed to dry in the dark. The dried spots are exposed, as in Example 1, for three minutes to the output from the high pressure mercury arc, filter through 5 cm of water and two Corning CSO-52 filters (short wavelength cut-off at 3,400 A.). The energy intensity of the incident radiation is 2.34×10^{-2} watts/cm². After exposure the control spot has a slight, but perceptible, blue coloration. The test spot has a strong blue color due to the incorporated dye. The filter paper is washed with acetone to remove both the unreacted diyne and soluble dye. In the process, the blue photoproduct is converted to a red form. The intensity of the red coloration of the test spot is much greater than that of the control spot. A dried test spot, utilizing sensitized diyne and prepared in the dark, is irradiated through a perforated masking sheet which is in contact with the filter paper. The same radiation source is used. After an exposure of 4 minutes, the filter paper is removed and washed with acetone. The resulting red image shows the perforations of the masking sheet.

Example 3

Drops of the test solution and the control solution used in Example 2 are placed on a filter paper and allowed to dry in the dark. The spots are then irradiated for 55 minutes with the output from the mercury arc, filtered through 5 cm of water, a Corning CS3-69 filter, and two Corning CSO-52 filters. The short wavelength cut-off is 5,100 A. and the incident energy intensity is 1.2×10^{-2} watts/cm². After exposure, the filter paper is washed with acetone to remove the unirradiated diyne and the thiapyrylium dye, and also to convert the blue photoproduct to a red form. The control spot has a slight, but perceptible, red coloration. The test spot shows a strong red coloration, indicating that the photoreaction in the sensitized spot is initiated by radiation with a wavelength greater than 5,100 A.

The following examples further illustrate the use of various pyrylium compounds, as well as different preparative techniques.

Example 4

A formulation of 3 ml of 12 percent aqueous gelatin solution, preservative, and 7cc distilled water is prepared. To this formulation are added 400 mg. of the monomethyl ester of 10,12-docosadiynedioic acid in 2cc of dichloromethane (gravity filter solution) and 10 mg of 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxyphenyl) thiapyrylium perchlorate in 1 ml dichloromethane.

The solution is dispersed in the gelatin formulation with an ultrasonic probe (60 second dispersion time) forming an oil-in-water emulsion. This emulsion is then placed on a rotary evacuator, 40°C bath, until all of the dichloromethane is removed. The volume of the disper-

sion is then adjusted to 10 ml with distilled water, and the dispersion is then coated at 10g/ft² on a subbed 4 mil poly(ethylene terephthalate) film support at about 21.5°C, chill set at 5°C, and air dried.

A wedge spectrogram exposure of this coating shows spectral sensitization to about 370 nm. (Native sensitivity of the polyacetylenic material extends to about 285 nm).

Examples 5 - 9

Solutions are prepared which contain 400 mg of the monomethyl ester of 10,12-docasadiynedioic acid dissolved in 1 ml of the indicated dispersion solvent, along with 3×10^{-5} moles of the indicated sensitizers. Each solution is then filtered into a solution of 4 ml of a 12 percent aqueous gelatin solution, 0.5 g of a 10 percent solution of Alkanol XC (a DuPont surfactant), 4.5 ml distilled water, and 3 drops of formalin. An oil-in-water emulsion is then formed by a 60 second disruption with an ultrasonic probe at maximum intensity, with a 1/2 inch tip. Each dispersion is then coated at 10 g/ft² on a polyethylene terephthalate film support overcoated with a conductive layer comprising cuprous iodide in cellulose nitrate (as disclosed by Trevoy U.S. Pat. No. 3,245,833), at 5°C, chill set (5°C) and air dried.

Example No.	Dispersion Solvent	Sensitizer	Spectrally Sensitive to
*5	cyclohexanone	None	approx. 285 nm
6	cyclohexanone	A	approx. 380 nm
7	dichloromethane	B	approx. 420 nm
8	cyclohexanone	C	approx. 500 nm
9	cyclohexanone	D	approx. 400 nm

*No formaldehyde is present in coating used in Example 5.

Sensitizers

- A. 2,4,6-Triphenylpyrylium fluoborate.
- B. 2,4,6-Triphenylthiapyrylium perchlorate.
- C. 2,6-diphenyl-4-(4-methoxyphenyl) thiapyrylium perchlorate.
- D. 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

Examples 10-14

Part A
monomethyl ester of 10,12-docosadiynedioic acid—4.512 g.

1,2-Dichloroethane—to 40 g net weight

Part B
Indicated sensitizer—10 mg
Indicated solvent—0.5 ml

2.5 ml of Part A are mixed with separate samples of Part B and the resultant solutions coated at .002 inch wet thickness on a 4 mil poly(ethylene-terephthalate) film support. The coating and drying temperatures are 80°F.

Samples of the above coatings are given wedge spectrogram exposures, and the following results observed.

Example Number	Sensitizer	Sensitizer Solvent	Spectrally Sensitive to
10	none	Methanol	300 nm
11	A	1:1 Methanol-acetone	560 nm
12	B	Methanol	510 nm
13	C	Methanol	510 nm
14	D	Methanol	560 nm

Example 15

Polyyne Dispersion
Part A
Monomethyl ester of 10,12-docosadiynedioic acid—12 g
Ethyl acetate—30 ml

Part B

12% aqueous gelatin solution—120 g

Alkanol XC (10% solution in 1:1 methanol-water—15 ml

Distilled water to a total weight of—300 g

Part A is added to Part B and the resultant mixture passed five time through a close tolerance colloid mill to effect homogenization. This dispersion is then chill set (35°F), cut into fine pieces, and dried in a room temperature forced air box for 2 days. This dried dispersion is then brought to a total weight of 270 g with distilled water, remelted at 40°C and then refrigerated for future use.

Coatings of polyne dispersion with spectral Sensitizer C

Nine gram samples of the polyne dispersion described above are placed in each of two tared 50 ml beakers containing a ½ inch magnetic stirring bar. The beakers are then placed in a 40°C water-bath and the dispersion allowed to melt, with stirring. When melted, 1.5 ml of methanol is added to one beaker and 15 ml of methanol containing 10 mg of Sensitizer C is added to the second sample with stirring. After five minutes, the net weight of the samples is adjusted to 10 g with distilled water. The dispersions are then coated as described in Example 4.

Wedge spectogram exposures of these coatings yield the following results.

Example Number	Sensitizer C	Spectrally Sensitive to
15A	none	300 nm
15B	yes	480 nm 520 nm

*Longer spectogram exposure.

Example 16

I. Formulation

Part A

Hexylammonium-20-(N-hexylcarbamoyl)-9,11-eicosadiyne-1-carboxylate—0.58 g

cyclohexanone—1 ml

Sensitizer C, (absent in Example 16A present in Example 16B 0.01 g

Part B

12% aqueous gelatin solution —4 ml

Alkanol XC (10% solution, 1:1 methanol-water—0.5 ml

Distilled water—4 ml

Parts A and B are homogenized and dispersed and coated as described in Example 4. The dispersions, however, are not placed in a rotary evacuator.

II. Testing of Examples 16A and 16 B

Wedge spectograms prepared on samples of the coatings above yield the following results.

Example Number	Sensitizer C	Spectrally Sensitive to
16A	none	300 nm
16B	yes	540 nm

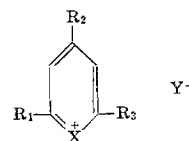
Representative pyrylium and thiapyrylium salts which are effective sensitizers for the photopolymerization of polyacetylenes have been reported. The nature of both the anion and cation may be varied within this particular class of salts to shift the absorption spectrum of the sensitizing dye and vary the efficiency of sensitization. In addition, a mixture of dyes

could be used in the sensitization of a single system. The sensitizers could be incorporated into a single layer containing the desired polyacetylene or into a multiple layer structure with the layers sensitized to different regions of the spectrum.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A composition comprising a radiation-sensitive crystalline polyacetylenic compound and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

- an aliphatic group having from 1 to 15 carbon atoms,
- an alkoxy group, and
- an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

Y is an anionic function.

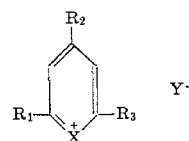
2. A composition as set forth in claim 1, wherein said polyacetylenic compound has a minimum of two acetylenic linkages as a conjugated system.

3. A composition as set forth in claim 1, wherein said polyacetylenic compound is selected from the group consisting of lower alkyl esters of diyne dioic acid, polyacetylenic polyoic acid alkylamides, polyacetylenic amine salts, and diyne diol urethanes.

4. A composition as set forth in claim 1, wherein said pyrylium compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxythiapyrylium) perchlorate, 2,4,6-triphenylthiapyrylium perchlorate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

5. A composition as set forth in claim 1, wherein said pyrylium compound is present in a concentration of from about 0.1 to about 50 percent by weight, based upon the weight of the polyacetylenic compound.

6. An element comprising a carrier, a radiation-sensitive crystalline polyacetylenic compound, and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

- an aliphatic group having from 1 to 15 carbon atoms,
- an alkoxy group, and
- an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

Y is an anionic function.

7. An element as set forth in claim 6, wherein said carrier comprises a support to which is adhered a binder having said polyacetylenic compound dispersed therein.

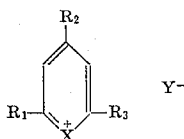
8. An element as set forth in claim 7, wherein said polyacetylenic compound has a minimum of two acetylenic linkages as a conjugated system.

9. An element as set forth in claim 8, wherein said binder is gelatin.

10. An element as set forth in claim 6, wherein said polyacetylenic compound is selected from the group consisting of lower alkyl esters of diyne dioic acid, polyacetylenic polyoic acid alkylamides, polyacetylenic amine salts, and diyne diol urethanes.

11. An element as set forth in claim 6, wherein said pyrylium compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxyppyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

12. An element comprising a carrier, a radiation-sensitive crystalline polyacetylenic compound having a minimum of two acetylenic linkages as a conjugated system, and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

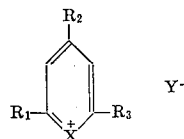
- an aliphatic group having from 1 to 15 carbon atoms,
- an alkoxy group, and
- an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

Y is an anionic function.

13. An element as set forth in claim 12 wherein said pyrylium compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxyppyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

14. An element comprising a support having coated thereon a layer comprising a binder, a radiation-sensitive crystalline lower alkyl ester of diyne dioic acid, and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

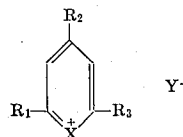
- an aliphatic group having from 1 to 15 carbon atoms,
- an alkoxy group, and
- an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

Y is an anionic function.

15. An element as set forth in claim 14 wherein said compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxyppyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

16. An element comprising a support having coated thereon a layer comprising a binder, a radiation-sensitive crystalline polyacetylenic amine salt, and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

- an aliphatic group having from 1 to 15 carbon atoms,
- an alkoxy group, and
- an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

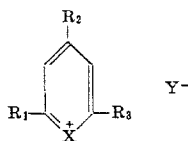
X is oxygen, sulfur or selenium and

Y is an anionic function.

17. An element as set forth in claim 16, wherein said compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxyppyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

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18. An element comprising a support having coated thereon a layer comprising a binder, a radiation-sensitive crystalline polyacetylenic alkylamide, and a sensitizing amount of a pyrylium compound of the formula:



wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

- a. an aliphatic group having from 1 to 15 carbon atoms,
- b. an alkoxy group, and
- c. an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

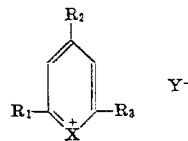
Y is an anionic function.

19. An element as set forth in claim 15, wherein said compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxypyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

20. An element comprising a support having coated thereon a layer comprising a binder, a radiation-

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sensitive crystalline polyacetylenic bis urethane, and a sensitizing amount of a pyrylium compound of the formula:



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wherein

R₁, R₂ and R₃ are each chosen from the class consisting of

- a. an aliphatic group having from 1 to 15 carbon atoms,
- b. an alkoxy group, and
- c. an aryl group chosen from the class consisting of phenyl, 4-biphenyl, alkylphenyl, alkoxyphenyl, ω-hydroxy alkoxyphenyl, 4-hydroxyphenyl, halophenyl, azidophenyl, nitrophenyl, and aminophenyl,

X is oxygen, sulfur or selenium and

Y is an anionic function.

21. An element as set forth in claim 17, wherein said bis urethane is 2,4-hexadiyne-1,6-diol bis (N-hexylurethane).

22. An element as set forth in claim 17, wherein said compound is selected from the group consisting of 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate, 4-(4-amyloxyphenyl)-2,6-bis(4-ethoxypyrylium) perchlorate, 2,4,6-triphenylpyrylium fluoborate, 2,4,6-triphenylthiapyrylium perchlorate, and 2,6-diphenyl-4-(4-dimethylaminophenyl) thiapyrylium perchlorate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,772,028 Dated November 13, 1973

Inventor(s) Sally S. Fico and Joseph W. Manthey

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

Page 2

Col. 15, line 34, "520 nm" should read ---520 nm*---.

Col. 19, line 26, "Claim 15" should read ---Claim 18---.

Col. 20, line 24, "Claim 17" should read ---Claim 20---.

Col. 20, line 26, "Claim 17" should read ---Claim 20---.

Signed and sealed this 19th day of November 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents