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E. C. LETTER
PHOTOSENSITIVE ELEMENT INCLUDING ELECTRON CONDUCTING
LAYER, ELECTRON SENSITIVE LAYER AND
PHOTOCONDUCTIVE LAYER
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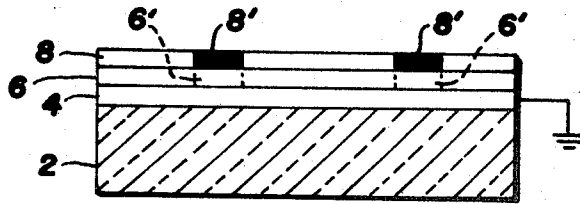


FIG. 1

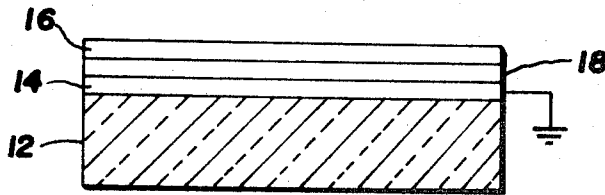


FIG. 2

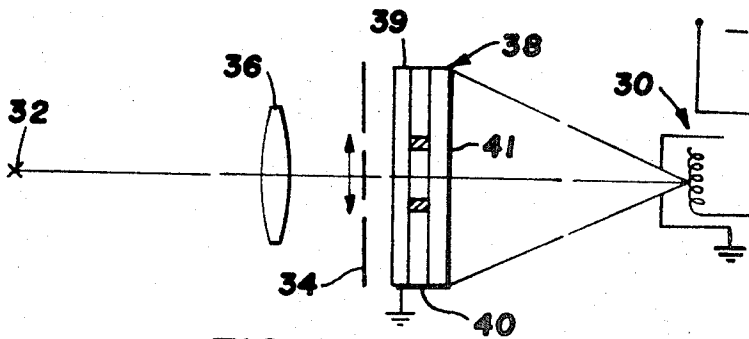


FIG. 3

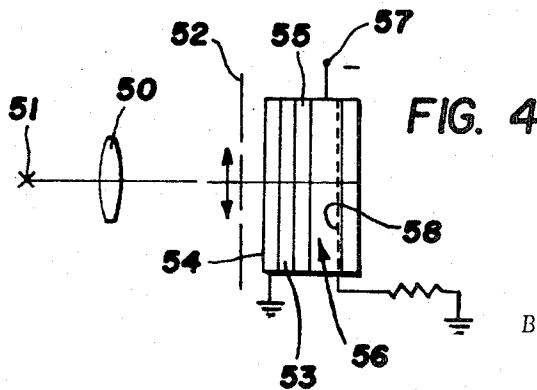


FIG. 4

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PHOTOSENSITIVE ELEMENT INCLUDING ELECTRON CONDUCTING LAYER, ELECTRON SENSITIVE LAYER AND PHOTOCONDUCTIVE LAYER

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Continuation-in-part of application Ser. No. 387,658, Aug. 5, 1964. This application Nov. 12, 1968, Ser. No. 774,891

The portion of the term of the patent subsequent to Nov. 21, 1984, has been disclaimed
Int. Cl. G03c 3/10; G03g 5/00

U.S. Cl. 96—1.8

5 Claims

ABSTRACT OF THE DISCLOSURE

A photoelectric element for recording information having three solid layers superimposed in contiguous relation including an electron conducting layer, an electron sensitive layer and a photoconductive layer. The photoelectric element is exposed to radiation to change the conductivity of the photoconductive layer in accordance to a desired pattern and is subsequently exposed to an electron beam to produce coloring in the electron sensitive film in accordance with the pattern of radiation received.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of my copending application Ser. No. 387,658, filed Aug. 5, 1964, now U.S. Pat. No. 3,455,683.

BACKGROUND OF THE INVENTION

The present invention relates to a novel photosensitive element which is particularly applicable for information recording and further to a novel method and apparatus for recording information.

The increased interest in the fields of electronics, computers, and high speed data recording and detecting systems has produced a demand for high speed high resolution films which are not only optically activated in accordance with the speed requirements but also may be electronically developed. The advantages of such films are numerous. For example, the chemical development and the accompanying apparatus and time delay as encountered in silver halide emulsions and other common photographic processes is eliminated since development is almost instantaneous by a completely dry process. Furthermore, the film's high resolution allows a relatively large amount of information to be stored on a relatively small area. Such features are particularly advantageous for aerial photography, data storage and other purposes.

The methods and apparatus for carrying out the present invention are relatively simple and may be produced and practiced in a manner which is presently thought to make these systems commercially competitive with conventional systems. Furthermore, the present elements, methods and apparatus are thought to be exceptionally versatile, so that their applications should extend over a wide range of potential uses. These uses extend from the very complex computer systems to the highly competitive office copiers.

SUMMARY OF THE INVENTION

Briefly, the photosensitive element according to the present invention comprises a multi-layer film. The film includes an electron sensitive layer, an electrical conducting layer and a photoconductive layer separating the electron sensitive layer from the electrical conducting layer. Preselected areas of the film are exposed to a light flux causing the photosensitive layer to become conductive. The electron sensitive film is then exposed to an electron

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bombardment of between 100–10,000 volts and preferably within the range of 1000–2000 volts. Those areas on the electron sensitive film which are electrically connected to the electron conducting layer by the exposed area of the photoconductive layer are preferentially colored by the electron bombardment. The apparatus for recording data will, therefore, include illumination means adapted to expose preselected areas of the element and means for bombarding the film with electrons.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a photosensitive element according to a first embodiment of the invention;

FIG. 2 is a cross-sectional view of an element according to a second embodiment of the invention;

FIG. 3 is a diagrammatic view illustrating apparatus for recording information according to one embodiment of the invention; and

FIG. 4 is a diagrammatic view illustrating another form of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A photosensitive element shown in FIG. 1 includes a substrate 2 or base for supporting a multi-layer film. The substrate may comprise a glass plate or in other cases may comprise a flexible film similar to the type commercially used for commercial photographic films. An electron conducting film 4 is disposed on the base 2 and may comprise, for example, a film of tin oxide, indium oxide, selenium oxide, or cadmium oxide or a thin semi-transparent coating of metal such as gold, copper, etc. On top of the layer 4 there is a photoconductive film 6. The film 6 may consist essentially of zinc oxide, lead oxide, cadmium sulfide, or other photoconductive material including the organic photoconductors. Any photoconductive material may be used, however, the selection of the photoconductive material depends in part on the spectral region of the actuating light flux. The thickness of the film 6 is determined by the material's dark conductivity, photoconductivity and by its optical properties such as absorption and index of refraction. For example, the dark conductivity must be sufficiently low to prevent the unexposed areas from coloring during exposure. The photoconductive film separates the electron conducting film 4 from an electron sensitive film 8 and its contiguous with both of the films 4 and 8.

The electron sensitive film may preferably comprise a lead fluoride film, or a film of $\text{PbO} \cdot \text{SiO}_2 \cdot \frac{1}{2} \text{PbF}_2$. The electron sensitive film may also comprise an alkali metal halide including the halides of lithium, sodium, potassium, rubidium and cesium or an alkaline earth halide including the halides of beryllium, magnesium, calcium, strontium and barium. The halides or oxides of copper, silver, gold, zinc, cadmium, mercury, gallium, indium, thallium, tin, lead, antimony and bismuth may also be used for the electron sensitive film. Those compounds having a relatively dark color will preferably be avoided since the change in optical density may be insufficient for some applications.

The alkali metal halides have been found to form F centers readily, see for example "Color Centers in Solids" by Schulman and Compton (Macmillan Co. 1962). Other centers including the colloidal centers may also be formed. The colloidal centers may be preferred in some cases since they produce a greater change in optical properties. For example, exposing a film of sodium chloride to electrons produces a yellow brown coloration due to the formation of F centers. Additional exposure of the yellow brown film to electrons changes the yellow brown color to a blue or blue violet color due to the formation of colloidal sodium centers.

The halides or oxides of the metals selected from the group consisting of copper, silver, gold, zinc, cadmium, mercury, gallium, indium, thallium, tin, lead, antimony and bismuth produce colloidal centers upon exposure to an electron beam which has a potential of 1000 to 5000 volts. It is also possible to combine the compounds of the latter group with each other or with the compounds of the first to form other satisfactory materials and to obtain particularly desirable properties. For example, a glass comprising $0.5 \text{ PbF}_2 \cdot 1 \text{ PbO} \cdot 1 \text{ SiO}_2$ also forms colloidal lead centers upon exposure to electron bombardment. In glasses of this type the mole fraction of the lead fluoride have been varied between 0.1 and 0.8.

It has been found that the film 8 may be colored by bombarding the film with electrons. However, only those areas 8' of the film 8 which are grounded by the exposed areas 6' will be colored by the electron bombardment. Accordingly, preselected areas of the film 6 are exposed to a light flux. Those areas may define an image of relatively high resolution. The light flux changes the electrical characteristics of the photoconductive film so that the conductance of the exposed areas increases relative to the intensity of the light flux. The exposed areas 6' become conductors and ground adjacent areas 8' of the electron sensitive film 8 by connecting those areas to the film 4. Accordingly, electron bombardment produces a dark color of unusually high resolution in those selected areas.

The elements described above may be produced by placing a glass substrate in a vacuum chamber and reducing the pressure therein to about 1 to 2 times 10^{-4} millimicrons or less and evaporating a metal layer such as aluminum, gold, copper or other conducting films onto the substrate. A photoconductive layer such as zinc oxide or lead oxide is built up onto the conductive layer. After a sufficient thickness is obtained a transparent layer of an electron sensitive film such as lead fluoride is evaporated onto the photoconductor. For fine resolution, evaporated photoconductive films are preferred to powdered, sintered or other films of coarse or grain structure. Additional details on photoconductive films are contained in the text of Richard H. Bube, "Photoconductivity of Solids," 1960, John Wiley & Son, and "Contact Influence on the Photoconductivity of Lead Oxide" by L. Heijne, *The Physics and Chemistry of Solids*, 22, 207-212, December 1961.

The element according to the first embodiment of the invention may be considered to be a transmitting element in its uncolored condition. Accordingly, a light source may be disposed on either side of the element and still operate effectively for exposing the photoconducting film 6. However, the source of electrons should be so constructed and arranged that the film 8 will be bombarded by the electrons.

In some cases it is also desirable to coat the bombarded film with an anti-reflecting film of magnesium fluoride. For example, in manufacturing a reticle for an optical system, the coating would not only improve the optical characteristics of the element, but would also improve its durability by providing a relatively hard film to thereby improve the scratch resistance of the element.

An element according to a second embodiment of the invention is shown more clearly in FIG. 2. The element is a reflecting element which may comprise a glass base 12 having a conducting film 14 deposited thereon. Even though the preferred form of the second embodiment includes a glass base, it is readily possible to use an aluminum or other metal plate as the first conducting layer. In that case the aluminum will act as a conducting film and as a suitable substrate. A photoconductive film 18 is deposited onto the conducting film 14 and separates the film 14 from an electron sensitive film 16.

Preselected portions of the film 18 are exposed to light to thereby render those portions conducting. The light

strikes the plate on the same side as the electron beam. Subsequent exposure to electron bombardment colors those portions of the film 16 which are grounded by means of the exposed areas of the film 18.

Interference effects have been obtained with various embodiments. In those cases the absorption characteristics together with the interference effects greatly enhance or increase the color change. These effects are most readily obtained with the reflecting elements, however, they may also be obtained in a transmitting element by proper choice of materials which have suitable indices of refraction and by applying those materials at predetermined thicknesses. The thicknesses and indices are selected in accordance with the conventional techniques used in manufacturing interference filters. In general the electron bombarded areas will have the highest indices of refraction of the multi-layer.

The apparatus shown more clearly in FIG. 3 includes a source of electrons 30 such as an electron gun. A light source 32 and means such as a movable mask 34 and objective lens 36 for exposing preselected areas of a photo-sensitive element 38 are provided. In other cases an image may be projected onto the film to thereby expose the pre-selected areas. In using the apparatus as a camera, the control of electrons or gas discharge may be used for the shuttering operation. Accordingly, the mechanical shutter may be eliminated in those cases wherein the electron sensitive material is not photosensitive.

The element 38 includes a transparent electrically conducting film 39 which is maintained at a positive potential with respect to the electron source and which is grounded, a photoconductive layer 40 and an electron sensitive layer 41. In some instances contrast may be imposed by biasing film 39. This is especially true where the conductivity of the photoconductive layer 40 is relatively high. By way of illustration, grounding through a suitable resistor (not shown) and biasing the conducting film 39 at -990 volts, if the voltage on the source filament is -1000 volts, the desired contrast can be achieved in layer 41. An electron bombardment changes the color of the layer 41 in those areas which are connected to the ground by means of the exposed photoconductive layer 40.

FIG. 4 illustrates another form of the invention wherein an objective lens 50, light source 51 and movable mask 52 are adapted to expose preselected areas of a photosensitive film 53 through a semi-transparent electrically conducting film 54 which is connected to ground. The exposed areas ground adjacent areas on an electron sensitive film 55. The film 55 is then bombarded by electrons and ions from a glow discharge within the cell 56. The gas pressure within the cell is between 1 to 50 microns to thereby facilitate the exposure of the electron sensitive surface to the discharge. Generally the cell is filled with an inert gas, however other gases and gaseous mixtures including air, nitrogen and hydrogen may be used. The electrons enter the cell by means of an electrode 57. In some cases a grid 58 is provided in order to obtain a more uniform bombardment. A transparent cell of this type may be illuminated from either direction however, the cell may incorporate a reflecting element. In those cases wherein a reflecting element is used, the grid should be so constructed and arranged that it does not adversely effect the illumination or readout steps.

While the invention has been described with reference to certain preferred embodiments, it should be understood that the invention may be modified or embodied in other forms without departing from the scope of the appended claims.

What is claimed is:

1. A photoelectric element comprising three solid layers superimposed in contiguous relation including an electron conducting layer, an electron sensitive layer selected from the group consisting of lead fluoride, and $\text{PbO} \cdot \text{SiO}_2 \cdot \text{XPbF}_2$ wherein X is within the range of 0.1 to 0.8 and a photoconductive layer responsive to radiation

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applied thereto for changing its conductivity in accordance with the amount of radiation received, said photoelectric element being responsive to electron flow therethrough to color said electron sensitive layer in accordance with the pattern of radiation received by said photoconductive layer.

2. A photoelectric element according to claim 1 in which the photoconductive layer comprises a thin film selected from the group consisting essentially of zinc oxide, lead oxide, cadmium sulfide or selenium.

3. A photoelectric element according to claim 1, which includes a glass substrate for supporting said films.

4. A method of storing information comprising steps of providing a photoelectric element including three solid layers superimposed in contiguous relation having an electron conducting layer, an electron sensitive layer selected from the group consisting of lead fluoride, and



wherein X is within the range of 0.1 to 0.8 and a photoconductive layer, responsive to light flux applied thereto for changing its conductivity in accordance with the amount of light flux received, illuminating preselected areas of the photoconductive layer to thereby change the conductivity of portions of the photoconductive layer and bombarding the photoelectric element with electrons to

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thereby change the color of the portions of the electron sensitive layer aligned with said preselected areas.

5. A method according to claim 4 in which the surface of the electron sensitive layer is subjected to a glow discharge of a potential of 1,000 to 2,000 volts.

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U.S. Cl. X.R.

96—1, 1.5, 27; 65—111; 106—53; 252—49.5, 83; 252—301.4