Nov. 21, 1961 C. F. WAHLIG 3,010,043

IMAGE STORAGE ELEMENTS AND PROCESS

Filed July 3, 1956

FIG. 1.

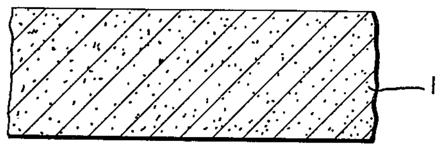

FIG. 2

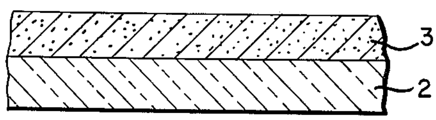

FIG. 3

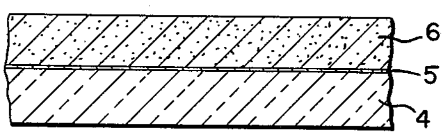

FIG. 4

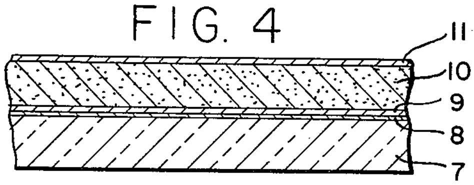

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IMAGE STORAGE ELEMENTS AND PROCESS

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This invention relates to an image storage element and to a process for image storage. More particularly, it relates to an image storage element comprising a layer of a binding material having embedded therein a radiation sensitive phosphor capable of image storage. Still more particularly, it relates to a process of imposing an image upon a radiation sensitive phosphor which may be in the form of a thin radiation sensitive element and subsequently causing said image to be released as visible light. Even more particularly, this invention relates to such a process and element wherein an electric field is utilized to release a stored image from a luminescent material. An important aspect of the invention is concerned with a process for imposing an image on a manganese-activated zinc sulfide phosphor by exposure of the phosphor to excitation radiation and subsequently releasing the stored image in an electric field, said process being carried out in the presence of a substantial amount of electromagnetic radiation.

As used herein, "image" is intended to mean any record, signal, etc., whether it be in the shape of a single small dot or a multiple of dots, squares, or other geometric form, a uniform exposure over the entire surface of the luminescent material, or a pattern, design or picture caused by exposing selected portions of a luminescent layer. The configuration of the image is not critical.

A system of convenient and effective image storage followed by release of the image under selected conditions has been long sought for many purposes. Such a memory system is of considerable utility, for example, in automatic calculators and computer equipment, wherein it is required to store an imposed signal for later release by predetermined conditions. Mechanical, magnetic and electronic devices for storage and release of images have been used with varying degrees of success. Of particular utility in such equipment and devices is an image storage element and more particularly a thin continuous tape having therein a material capable of receiving and subsequently releasing an imposed image.

It is an object of the present invention to provide an element for image storage. Another object is to provide a storage element containing luminescent material capable of storing an imposed image and subsequently releasing it as visible light. Still another object is to provide such a storage element in tape form adapted for use in automatic calculators, computers and memory devices. An additional object is to provide such a storage element which is insensitive to heat, infrared radiation and daylight. Yet another object is to provide such a tape useful in carrying out the novel processes according to this invention.

In addition to the above, it is an object of the present invention to provide a process for image storage. Another object is to provide a process for storing an image and later releasing it as visible light. Still another object is to provide such a process which can be effectively performed in the presence of electromagnetic radiation of a wave length longer than about 500 millimicrons, including infrared and most of the visible light spectrum. Yet another object is to provide such a process wherein the image storing element is characterized, while storing the image, by substantial insensitivity to infrared as well as red, orange, yellow and some green radiation of the

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light spectrum. Another object is to provide such a process wherein the image storing element is characterized, while storing the image, by substantial insensitivity to variations in ambient temperature, including elevated temperatures, and substantial insensitivity to moisture and other surroundings usually considered unfavorable to image storage processes. An additional object is to provide such a process wherein the storage material enables almost immediate release, as well as release after a prolonged period of time, of the stored image as visible light. A further object is to provide such a process which permits quick erasure of the imposed image and prompt reuse of the storage material. A still further object is to provide such a process which is relatively simple and of considerable utility in the art.

In an important aspect, the novel storage element of this invention is a thin continuous tape comprising a thin layer containing a luminescent material and a binder for said luminescent material, wherein said luminescent material is characterized by meeting the requirements of the following test, which is carried out in its entirety in the presence of electromagnetic radiation of wave length longer than about 500 millimicrons: namely, that after subjection of the luminescent material to excitation radiation while the luminescent material is within an electric field of a strength of less than about 50,000 volts per centimeter, thus imposing an image on the luminescent material, and upon subsequent subjection to an electric field of strength at least as great as that of the first-mentioned field, said luminescent material exhibits an emission of visible light as it releases the image.

In a preferred embodiment, the novel storage element of the invention is a tape comprising a transparent flexible support bearing on its surface a layer of a binding material containing a luminescent phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfied containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing activating manganese in an amount of from about 0.2% to about 2.0% by weight of said metal sulfide.

In another preferred embodiment, the novel storage element of the invention comprises a layer of a binding material containing a luminescent phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing activating manganese in an amount of from about 0.2% to about 2.0% by weight of said metal sulfide, which phosphor in said layer is shielded from external blue and ultraviolet electromagnetic radiation by a suitable filter dye which may be in said layer or in separate layers on each side of said layer, said filter dye permitting the transmission of X-rays.

The process of the invention is carried out by imposing an image upon a phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing activating manganese in an amount of from about 0.2% to about 2.0% by weight of said metal sulfide. The image is imposed, i.e., the phosphor is made to receive the image, by subjecting the phosphor to excitation radiation while the phosphor is within an electric field of a strength of less than about 50,000 volts per centimeter. Release of the stored image is obtained by subsequently subjecting the phosphor to an electric field of a strength at least as great as and preferably greater than that of the first-mentioned field. Utilization of the metal sulfide phosphor referred to above results in an image of outstanding intensity.

The expression "excitation radiation," as used in this application to identify the stimulus used to impose the image on the phosphor, broadly covers exciting stimuli to which the phosphor is initially sensitive, and specifically includes electromagnetic radiation of a wave length shorter than about 500 millimicrons, e.g., visible blue light, ultraviolet radiation, X-rays, gamma rays and cosmic rays, and also alpha particles, i.e., positively-charged helium nuclei, and beta particles, i.e., negatively-charged particles, e.g., electrons, such as are emitted from radioactive substances. Excitation radiation does not include electric fields or electromagnetic radiation of wave length longer than about 500 millimicrons, such as infrared radiation, since the phosphor utilized in this process is not excitable by these means.

The term "electric field" is well known in the art to describe the action of electrical forces exhibiting a potential gradient, i.e., a change of potential, or voltage, per unit distance. The magnitude of an electric field is herein expressed as field strength but is also called field intensity or simply electric field.

In an important aspect of the process of the invention, during which the process is carried out in the presence of electromagnetic radiation of wave length longer than about 500 millimicrons, e.g., infrared, red, orange, yellow and some green light radiation, a phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfied and zinc cadmium sulfied containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing activating manganese in an amount of from about 0.2% to about 2.0% by weight of said metal sulfide, is subjected to excitation radiation, thereby causing said phosphor to luminesce, while within an electric field of a strength of less than about 50,000 volts per centimeter, and, after visible phosphorescence has fallen to a negligible intensity, subjecting said phosphor to an electric field of a strength at least as great as and preferably greater than that of the first-mentioned field, thereby causing said phosphor to emit visible yellow-orange light.

In a preferred process for carrying out the invention, a zinc sulfide phosphor containing activating manganese in an amount of from about 0.2% to about 2.0% by weight of the zinc sulfide is irradiated with, i.e., exposed to the action of, excitation radiation, whereby said phosphor exhibits emission of visible light, and, after said irradiation and after said emission of visible light has essentially ceased, said phosphor is subjected to an electric field, whereby said phosphor again exhibits emission of visible light, the entire process being carried out in the presence of visible light of wave length longer than about 500 millimicrons.

In a preferred embodiment of the process of the invention, utilizing the manganese-activated metal sulfide phosphor referred to above wherein the phosphor is in the form of a layer which may include a binder for the phosphor, selected portions of the layer are subjected to excitation radiation, thereby imposing a latent image in the layer. The layer is subsequently subjected to one or more electric fields according to this invention thereby causing the stored or latent image to become visible in the form of emitted yellow-orange light. As stated above, utilization of the metal sulfide phosphor referred to above results in an image of outstanding intensity.

In a second preferred embodiment of the process of the invention, the phosphor referred to above is exposed through a radiation selective filter material, e.g., ultraviolet and/or blue absorbing dye, to excitation radiation, e.g., X-rays, transmittable by said filter element, and subsequently subjected to an electric field.

In all embodiments of this invention, an important feature resides in the step of applying an electric field which causes the phosphor to emit the stored image as visible light. This release of visible light may occur once or a number of times, on successive applications of electric fields to the phosphor. It has been found that flashes of light upon release of the stored image will be of greater brightness and of controllable intensity if the applied fields are of successively greater strength, and such is therefore preferred. However, successive applications of fields of equal strength will produce a multiple of image flashes of decreasing intensity and such is contemplated within the scope of the invention, as illustrated by Example X.

The manganese content of 0.2% to 2.0% is critical for carrying out the process of this invention. Although the general luminescent properties of manganese-activated zinc sulfide and zinc cadmium sulfide phosphors are of considerable utility over a much broader range of manganese content, it has been found unexpectedly that, in the process of the present invention, the visible emission of the phosphor upon application of the field releasing the image is of a satisfactory intensity only within the critical manganese range. It has also been unexpectedly found that the amount of cadmium should not exceed the limit stated above in order to result in a satisfactory image intensity.

Surprisingly, it has been found that the process of this invention, when limited to the particular luminescent phosphor referred to above with its critical range of manganese content, is unhampered when carried out in the presence of electromagnetic radiation of wave length longer than about 500 millimicrons. The presence of such electromagnetic radiation, e.g., infrared, subdued daylight or similar visible portions of the electromagnetic radiation spectrum exhibiting relatively little blue and ultraviolet radiation, does not interfere with the ability of the phosphor to retain an imposed image and subsequently release the image upon exposure of the phosphor to an electric field. It has been found unexpectedly that the presence of such radiation does not "kill" the ability of the phosphor to produce the image then being stored upon application of an electric field, and of course its ability to receive, store and subsequently release another image is unimpaired. It has also been found unexpectedly that irradiation of the phosphor with infrared light while the phosphor is storing an imposed image does not cause the phosphor to release the stored image.

Representative storage elements of this invention are shown in the accompanying drawing which forms a part of this application. Referring now to the drawing:

FIG. 1 is a schematical cross-section of the image storage element described in Example XVIII;

FIG. 2 is a schematical cross-section of the image storage tape described in Example XIX;

FIG. 3 is a schematical cross-section of the image storage tape described in Example XX; and

FIG. 4 is a schematical cross-section of the image storage element described in Example XXVIII.

The present invention will be further illustrated and explained but is not intended to be limited by the following examples:

Example I

In a darkened room, 5 samples of a zinc sulfide phosphor powder containing manganese in an amount respectively of 0.2%, 0.5%, 1.0%, 1.5% and 2.0% by weight of the zinc sulfide are used to form phosphor panels by placing each of the samples between two thin sheets of electrically-conductive glass. The panels of phosphor samples are each exposed for one minute to ultraviolet radiation of wave length of approximately 365 millimicrons from a high-pressure mercury-vapor arc lamp. During this ultraviolet light exposure, each of the phosphor samples emits clearly visible yellow-orange light, which persists for approximately 3 to 5 seconds after the ultraviolet source is removed. After about 10 minutes, an electric field having a strength of 50,000 volts per centimeter is applied to the phosphor samples by connecting each of the two sheets of conductive glass for each panel to a battery source, whereupon each of the samples emits a clearly visible yellow-orange light flash.

Example II

Example I is repeated six times except that the period of delay between the application of the ultraviolet light and the electric field is respectively 15 seconds, 10 minutes, 1 hour, 5 hours, 15 hours and 18 hours. In each instance, the application of the field causes a clearly visible yellow-orange light flash.

Example III

Example I is repeated two times, except in a slightly darkened room, illuminated by subdued diffused daylight, and the period of delay between the application of the ultraviolet light and the electric field is respectively 30 seconds and 3 minutes. In each instance, the application of the field causes a clearly visible yellow-orange light flash.

Example IV

Examples I and II are repeated, except that each of the phosphor samples is subjected to an electric field of 20,000 volts per centimeter up to the time the field of 50,000 volts per centimeter is applied. Application of the latter field causes each of the phosphor samples to emit a clearly visible yellow-orange light flash, which is of slightly lower intensity than in the preceding examples.

Example V

Example IV is repeated, except that the strength of the first-mentioned electric field is 1,000 volts per centimeter and the strength of the last-mentioned field is 10,000 volts per centimeter, with results observed as in the preceding example.

Example VI

Example IV is repeated except that each of the phosphor panels is prepared by mixing the phosphor powder samples with a high-dielectric-constant thermo-setting urea-formaldehyde/alkyd resin binder and flowed onto a transparent electrically-conductive glass sheet to form a layer about 20 mils thick. After flash-drying for 15 minutes and heating in an oven at 90° C. for 1½ hours, the coating is 7–8 mils thick. A layer of conductive silver is painted on the exposed binder surface. The strength of the first-mentioned electric field is 45,000 volts per centimeter and the strength of the last-mentioned field is 100,000 volts per centimeter, which fields are applied to the samples by connecting the sheet of conductive glass and the conductive silver layer of each panel to a battery source. For each sample, application of the latter field causes the emission of a clearly visible yellow-orange light flash.

Example VII

Example III is repeated except that the ultraviolet light source is replaced with an X-ray source containing a copper target, operated at 50 kilovolts and 15 milliamperes for 10 seconds. Subsequent application of the electric field causes each phosphor sample to emit a clearly visible yellow-orange light flash.

Example VIII

Example II is repeated except that the ultraviolet light source is replaced with a 10 millicurie strontium-90 source of beta particle radiation placed at a distance of one inch from each sample for 10 seconds. Subsequent application of the electric field causes each phosphor sample to emit a clearly visible yellow-orange light flash.

Example IX

Example II is repeated except that the ultraviolet light source is replaced with a 5 millicuries cesium source of gamma radiation placed 0.5 inch from each phosphor sample for 125 seconds. Subsequent application of the

electric field causes each phosphor sample to emit a clearly visible yellow-orange light flash.

Example X

Example IV is repeated except that the last-mentioned field is of a strength of 25,000 volts per centimeter, followed successively at intervals of approximately 15 seconds by the application of four additional electric fields of strength respectively of 25,000, 40,000, 40,000 again and 50,000 volts per centimeter. For all phosphor samples, application of each of the five last-mentioned fields causes the emission of a clearly visible yellow-orange light flash.

Example XI

Example VI is repeated, except that the strength of the last-mentioned field is 75,000 volts per centimeter, followed successively at intervals of approximately 5 minutes by the application of fields having a strength respectively of 100,000 and 120,000 volts per centimeter. For all phosphor samples, application of each of the three last-mentioned fields causes the emission of a clearly visible yellow-orange light flash.

Example XII

Examples II, V, VI and VII are repeated except that each of the 5 phosphor samples is zinc cadmium sulfide containing about 4 mol percent cadmium based on the total amount of zinc and cadmium, and containing manganese in an amount of 0.2%, 0.5%, 1.0%, 1.5% and 2.0% respectively by weight of the zinc cadmium sulfide. In each instance the observed results are the same as those of the respective examples.

Example XIII

Examples II, V, VI and VII are repeated except that each of the 5 phosphor samples is zinc cadmium sulfide containing about 6½ mol percent cadmium based on the total amount of zinc and cadmium, and containing manganese in an amount of 0.2%, 0.5%, 1.0%, 1.5% and 2.0% respectively by weight of the zinc cadmium sulfide. In each instance the observed results are the same as those of the respective examples.

Example XIV

Example VII is repeated except that the room is brightly illuminated by unfiltered daylight with the samples protected from ultraviolet and blue light exposure by a Wratten No. 8 gelatin filter (K2) which transmits only electromagnetic radiation of a wave length longer than about 500 millimicrons, including infrared, red, orange, yellow and some green light. The observed results seen through the filter are the same as in that example.

Example XV

Example II is repeated except that the ultraviolet light source is replaced with a monochromator source emitting a bluish violet light of a wave length of approximately 435 millimicrons. The observed results are the same as in that example.

Example XVI

Example II is repeated except that the exposure to ultraviolet light is replaced by an exposure of each of the samples to unfiltered daylight. For each sample, application of the electric field causes a clearly visible yellow-orange light flash.

Example XVII

Example VI is repeated, wherein the panel containing the mixed phosphor and binder is approximately 6 inches long and 6 inches wide. Each of the panels is exposed for about 30 seconds to unfiltered daylight on the conductive-glass side of the panel through a black stencil design image painted on a transparent glass sheet. In each instance, subsequent application of the electric field causes the emission of yellow-orange light in a pattern corresponding to the transparent areas of the stencil image.

Example XVIII

The following ingredients are mixed for one-half hour in a double-arm mixer:

400 g. of a 25% solution in toluene of a chlorosulfonated polyethylene containing approximately 27.5% chlorine and 1.5% sulfur, wherein most of the chlorine is substituted along the hydrocarbon chain and the sulfur is combined with chlorine and attached to the carbon chain as sulfonyl chloride (SO_2Cl);
400 g. luminescent manganese-activated zinc sulfide containing manganese in an amount of 0.4% by weight of the zinc sulfide;
10 g. stearic acid;
15 g. magnesium oxide; and
1 g. 2-mercaptoimidazoline.

The resultant dispersion is filtered through nainsook, deaerated, cast onto a polished chromium-plated surface and dried to obtain a film 0.010 inch thick and several feet square. The film is then stripped from the casting surface, vulcanized at 300° F. for 30 minutes, and subjected to the test described for the phosphor panels in Example I. The luminescent material in the self-supporting film layer emits a clearly visible yellow-orange light flash. The storage element of this example as stated above is illustrated in FIG. 1 of the drawing. Referring now to this figure, the storage element comprises a single self-supporting layer **1** of the luminescent phosphor material dispersed in the chlorosulfonated polyethylene binder composition.

Example XIX

Thirty grams of luminescent manganese-activated zinc sulfide containing manganese in an amount of 0.2% by weight of the zinc sulfide is stirred by hand into 8 g. of the chlorosulfonated polyethylene solution in toluene of Example XVIII, to which 8 ml. toluene is added. The resultant dispersion is cast on polyethylene terephthalate film 4 mils thick, 35 mm. wide, 10 feet long and having cine perforations along both edges of the film. The coating after drying is about 0.0035 inch thick. When tested by the process described in Example XIV, the luminescent material in the coated layer emits a clearly visible yellow-orange light flash. The image storage tape of this example is illustrated in FIG. 2 of the drawing. Referring to this figure, the polyethylene terephthalate film support **2** has coated thereon the phosphor-binder layer **3**.

Example XX

To a perforated polyethylene terephthalate film 4 mils thick and 1 inch wide, having coated thereon a thin layer of vinylidene chlorine copolymer, which coated film is described in Alles and Saner U.S. Patent No. 2,627,088, is applied a dispersion of manganese-activated zinc sulfide phosphor in a chlorosulfonated olefin addition polymer as described in Example XVIII. The phosphor contains manganese in an amount of 1% by weight of the zinc sulfide. The phosphor in the binder layer is applied by the doctor blade method to obtain a dry film thickness of 4 mils. When tested by the process described in Example XIV, the phosphor material in the coated binder layer emits a clearly visible yellow-orange light flash. The image storage tape of this example is illustrated in FIG. 3 of the drawing, in which the polyethylene terephthalate film **4** with its vinylidene chloride copolymer coating **5** bears as a surface coating the phosphor-binder dispersion **6**.

Example XXI

Example XVII is repeated using the image storage tape of Example XIX in place of the panels. The observed results are the same as in Example XVII.

Example XXII

The following ingredients are mixed by ball milling for 2 hours:

30.0 g. luminescent manganese-activated zinc sulfide containing manganese in an amount of 1% by weight of the zinc sulfide;
1.0 g. epoxidized soya oil having a molecular weight of about 1,000;
6.0 g. of a 25% solids solution of cellulose nitrate in methanol; and
0.3 g. of the dioctyl ester of sulfosuccinic acid in 5.0 ml. toluene and 5.0 ml. methanol.

The resultant dispersion is filtered through two layers of nainsook and coated by means of a doctor blade on a layer of cellulose acetate sheeting 0.005 inch thick. A strip of the coated sheet is exposed to the ultraviolet light source of Example I through a stencil pattern of dots. After about 15 minutes, the strip is placed between two sheets of conductive glass plate, between which plates is applied an electric field of a strength of about 20,000 volts per centimeter. Upon application of the field, the dot pattern is clearly perceptible as the areas which have been irradiated with the ultraviolet light simultaneously emit a flash of yellow-orange light.

Example XXIII

Example XXII is repeated in a moisture-free atmosphere except that the binder for the 30.0 g. of phosphor has the following composition:

20 g. of 10% aqueous solution of medium viscosity (4% aqueous solution at 20° C., 23–28 centipoises) polyvinyl alcohol;
10 ml. distilled water; and
1 g. Turkey red oil.

The results are the same as observed in that example.

Example XXIV

Example XXII is repeated except that the binder for the 30.0 g. of phosphor has the following composition:

8.0 g. of a 25% solution in methanol of polyvinyl butyral having a 2.5 residual polyvinyl acetate and 19% hydroxyl content calculated as polyvinyl alcohol;
0.5 g. stearic acid; and
0.5 g. of the dioctyl ester of sulfosuccinic acid in 5.0 ml. butanol and 5.0 ml. toluene.

The results are the same as observed in that example.

Example XXV

Example XXII is repeated except that the binder for the 30.0 g. of phosphor has the following composition;

65 g. of a 10% solution of high viscosity polyvinyl acetate in amyl acetate; and
10 g. acetone.

The results are the same as observed in that example.

Example XXVI

To the phosphor-binder composition of Example XXIV is added 0.025 g. Tartrazine dye (Colour Index 640) and 0.025 g. beta-naphthol-6,8-disulfonic acid, each in the form of its alcohol-soluble di-o-tolylguanidine salt. The resultant composition is coated on cellulose acetate sheeting as in Example XXII to form a storage element, which is then exposed through a stencil pattern of dots to an X-ray source as described in Example VII. The storage element containing the stored image pattern is handled in full daylight and after 45 minutes is placed between 2 plates of conductive glass. An electric field of a strength of about 16,000 volts per centimeter is applied between the plates, and the dot pattern image is revealed clearly as a flash of yellow-orange light. To make a permanent photographic record of the image, a second electric field of a strength of about 48,000 volts per centimeter is applied while a standard negative light-sensitive photographic film element is adjacent the storage element. Subsequent developing and fixing of the negative film, followed by printing according to well known procedures, result in a permanent positive image record of the original dot pattern. As in Example XIX, the storage element is illustrated in FIG. 2 of the drawing.

Example XXVII

Example I is repeated except that after the ultraviolet light exposure and 10 minute delay, the panels are subjected to intense infrared radiation for 5 minutes from a 60 watt tungsten lamp located at a distance of 10 inches through two infrared filters in series (Wratten No. 87 and No. 87C gelatin filters). Subsequent application of the electric field as described in Example I results in each of the samples emitting a clearly visible yellow-orange light flash.

Example XXVIII

To a polyethylene terephthalate film having a vinylidene chloride copolymer coating, as in Example XX, is applied a dispersion of 0.06 g. Tartrazine dye (Colour Index 640) and 0.06 g. beta-naphthol-6,8-disulfonic acid in a binder of 1.0 g. epoxidized soya oil (molecular weight ca. 1000), 6.0 g. of a 25% solids solution of cellulose nitrate in methanol, and 0.3 g. of the dioctyl ester of sulfosuccinic acid in 5.0 ml. toluene and 5.0 ml. methanol, to provide a dry layer thickness of 0.0005 inch. Upon this layer is applied a dispersion of 30 g. of luminescent manganese-activated zinc sulfide containing manganese in an amount of 0.2% by weight of the zinc sulfide, 8 g. of the chlorosulfonated polyethylene-toluene solution of Example XVIII and 8 ml. of toluene, to provide a dry layer thickness of 0.0035 inch. Over the phosphor-binder layer is coated a second dye-containing layer as described in this Example XXVIII, which also serves as an anti-abrasion layer. With full daylight handling, the storage element is tested according to the process described in Example XXVI with similar observed results. The image storage element of this example is illustrated in FIG. 4 of the drawing, in which the polyethylene terephthalate film 7 with its copolymer coating 8 bears in turn dye layer 9, phosphor-binder layer 10 and dye layer 11.

Methods for preparing the phosphors used in the storage element and process of this invention are known in the art. According to one such method, the dry sulfide or mixtures of zinc sulfide and cadmium sulfide, together with the desired amount of manganese, is fired by baking at an elevated temperature, followed by washing, drying and sieving. The sulfides must be of a high order of purity and can be obtained by precipitation from solutions as described in Nitsche U.S. application Serial No. 421,191, filed April 5, 1954, now U.S. Patent No. 2,805,917. The manganese can be conveniently introduced in the form of compounds of manganese, such as $MnCl_2$, MnS and $MnSO_4$. The phosphor preparation can take place in the presence of a suitable flux, such as $BaCl_2$ $CaCl_2$, $SrCl_2$, NaCl, NH_4Cl, NaBr, $MgSO_4$ or mixtures of such compounds, or in the absence of a flux, as is well known in the art.

Firing for 30 minutes or longer at temperatures above 550° C. will produce the luminescent phosphor, which may be of a cubic or hexagonal crystalline structure, with the cubic structure preferably predominating. Firing may be followed by a wash with water, HCl, KCN or other known rinsing solutions, after which the phosphor material can be dried and sieved.

During the process of this invention, the phosphor may be used as a dry powder or the phosphor may be mixed with a suitable binder, as illustrated by the examples. Use as a dry powder has the advantage of contributing to a less expensive, simpler and quicked process than when a binder is used. However, it has been found that electric fields of higher strengths, e.g., 70,000 volts per centimeter and above, can be used more successfully when the phosphor-binder mixture is used.

Suitable binding agents utilizable in the process and the storage element of this invention include polymeric materials, for example, a cellulose derivative such as cellulose acetate, cellulose nitrate, cellulose acetate-propionate; a synthetic resin or super polymer, e.g., a polymethyl methacrylate/phenol-formaldehyde condensation product, polystyrene, nylon, vinylidene chloride copolymers with ethylenically unsaturated monomers, e.g., vinyl chloride, vinyle acetate, isobutylene, acrylonitrile, etc. The binding materials can be used as fluids or as solutions in suitable organic solvents. The preferred binder material is a chlorosulfonated olefin addition polymer of the type described in U.S. Patents Nos. 2,212,786, 2,416,060 and 2,416,061 and more particularly a chlorosulfonated addition polymer of an olefin containing 1 to 2 olefinic bonds and not more than 5 carbon atoms, of the type described in Alles U.S. application Serial No. 512,282, filed May 31, 1955, now U.S. Patent No. 2,819,183.

In the preferred embodiment of the process, wherein the phosphor material is in the form of a layer, and in the storage element of this invention, the phosphor layer may be self-supporting, as illustrated by Example XVIII and FIG. 1 of the drawing, or it may be joined to a base support as illustrated by Examples XIX, XX and XXVIII and FIGS. 2–4. In the latter cases, this support is preferably flexible and may consist of such well known film-forming materials as cellulose derivatives, e.g., cellulose nitrate, cellulose triacetate, cellulose propionate, cellulose acetate butyrate, polyvinyl chloride, polyvinyl chloride/acetate; polyamides; polyvinyl acetals, e.g., from formaldehyde and acetaldehyde; super polyesters from dicarboxylic acids and dihydric alcohols, e.g., oriented sheets of polyethylene terephthalates having melting points above 200° C. The latter is the preferred support material because of its strength, stability and other desirable physical properties. Other suitable supports are paper, glass, metals, closely woven fabrics, etc.

As used herein, the expressions "element" and "storage element" are intended to mean any article comprising the phosphor storage material according to this invention. The terms specifically include self-supported phosphor-binder layers, as well as layers of the phosphor material, with or without binder, adjacent and/or joined to the base supports, which may be flexible or rigid, flat or otherwise shaped, e.g., sheets, plates, screens, strips, bands, wires, panels, drums, disks, belts, etc. The precise shape of the image storage element is not critical and will be determined by the desired use. The preferred storage elements are thin narrow long elements herein referred to as tapes. For convenience in handling or conveying, the element in tape form may be perforated along one or both edges, as will be known to persons skilled in the art.

A wide range of electric field conditions can be used in the process of this invention. The field may be applied from a source of potential such as a battery. Alternating pulse fields of 25 to 500,000 cycles per second or higher of a strength or intensity as high as 100,000 to 150,000 volts per centimeter or higher are suitable. The frequency and voltage used in any situation are readily determinable by persons skilled in the art and depend on such factors as the density of the phosphor particles, the thickness of the phosphor layer, the electrical properties of the binding material where such is used, the particular construction of the phosphor panel or tape, the desired emission intensity, etc.

As is stated above, the phosphor is subjected to excitation radiation while within an electric field of a strength of less than about 50,000 volts per centimeter.

This range of electric field strength is intended specifically to include the situation where the field strength is zero, i.e., where no electric field is applied. Applying an electric field to the sulfide phosphor while it is being exposed to excitation radiation has the distinct advantage of permitting the subsequent application of fields of strength less than that of the first-mentioned field without effecting the release of a visible flash of light. Such a process is of considerable use in the art of memory devices and processes, wherein it is often desired to release a stored signal only when an applied release-stimulation exceeds a certain level. Not applying an electric field to the sulfide phosphor while it is being exposed to excitation radiation has the advantage of permitting the subsequent release of the stored image by the application of a field of low strength, and is particularly advantageous when the intensity of the excitation radiation is low.

The upper limit of 50,000 volts per centimeter as the strength of the field applied during exposure of the phosphor to the excitation radiation is selected as a practical limit. Application of the field during exposure limits the intensity of the amount of energy that can be stored and later released. It has been found that above 50,000 volts per centimeter less than about 10% of the energy of the imposed radiation will be stored and released. It will therefore be understood that this upper limit is not critical, but rather represents an approximate practical value in a decreasing scale of energy storage efficiency.

The period of delay from the time of the exposure of the phosphor to the excitation radiation until the time a subsequent electric field is applied may vary from a few seconds to as high as twenty hours or more. Application of the field used in the process of this invention to release the flash of light, i.e., the stored image, will preferably occur after the visible phosphorescence of the excited phosphor has fallen to a negligible intensity, although, as mentioned above, application of the field before cessation of phosphorescence results in a flash of outstanding intensity when the metal sulfide phosphor described herein is utilized. In cases where serveral applications of fields are used, the time period between each successive application may be as high as 20 hours or more.

Erasure or partial erasure of a stored image can be easily and quickly effected so that the phosphor, preferably in tape form as stated above, may be reused in the process of the invention by applying in rapid succession a multiple of preferably increasing fields to the phosphor, or by applying a stronger field than that used for viewing, thus causing emission and release of the stored image.

It is obvious that storage elements comprising the phosphor utilized in this invention may be made to receive a picture or stencil image which can be subsequently released as visible light by exposing the storage element to the excitation radiation through the object which it is desired to reproduce. An outstanding advantage of such a feature, which is illustrated by Examples XVII and XXII-XXVI, is that the process presents the opportunity to inspect the image for quality upon application of the electric field, followed by printing of the image, e.g., by photopgraphic means, if the image is satisfactory, as illustrated by Example XXVI. If unsatisfactory, the image can of course be promptly erased as described above and the process repeated.

An outstanding feature of this invention is illustrated by Examples XXVI and XXVIII, wherein utilization is made of a filter dye such as is well known in the art and which has the characteristic of allowing the transmission of radiation of certain wave lengths while preventing the transmission of other radiation. The filter material, e.g., dye, may be within the same layer as the phosphor, as described in Example XXVI, or in separate adjacent layers on each side of the phosphor layer, as described in Example XXVIII. Such a structure makes it possible to favor one form of excitation over another. These examples illustrate the use of a filter dye which absorbs blue and ultraviolet light but permits the transmission of electromagnetic radiation of wave lengths longer than 500 millimicrons, and more penetrating shorter wave length electromagnetic radiation, e.g., X-rays, gamma rays, etc. Such a storage element can be used in full daylight during imposition of the image, storage and subsequent image release. Various dyes can be used and can be readily selected by persons in the art. Suitable ultraviolet-absorbing dyes include beta-naphtholdisulfonic acid, the sodium salt of beta-naphtholdisulfonic acid, umbelliferone, acridine, and 2,2′-dihydroxy-4,4′-dimethoxybenzophenone. Suitable blue-absorbing dyes include Tartrazine (Colour Index 640), Auramine O (Colour Index 655) and p-nitrophenol at a pH of about 10. Mixtures of dyes can of course be used.

Similarly, the use of a filter dye within this invention includes the use of a dye which transmits blue light but absorbs ultraviolet. This feature causes the subsequently released image to appear more natural to the viewer, i.e., more nearly like that which is seen by the human eye in daylight. Suitable dyes can be readily selected for a particular purpose and the above-mentioned dyes are intended only to be illustrative and not limitative.

Other means of selective radiation transmission are of course available. For example, a metal sheet on one side of a phosphor layer could be ultilized to transmit X-rays and the image could be observed on the non-metal side of the phosphor layer upon application of the image-releasing electric field. Similarly, a layer which is highly reflective of the visible light emitted, e.g., titanium dioxide in a suitable binder, could be coated on a thin flexible film support. Such a reflecting layer could serve in place of the metal sheet to selectively transmit X-rays but not other undesired radiation.

The flash of visible light upon image release may be utilized in many ways. It may be observed by an operator as a signal to perform some task. It may energize a photoelectric device which transfers the signal according to well known procedures.

An outstanding advantage of the process and storage element of this invention lies in the unusual heat-insensitivity of the manganese-activated metal sulfide phosphors described above. For example, application of a substantial amount of heat, e.g., 200–300° C., to the phosphors does not interfere with their image-storage ability and image-release ability. Application of heat during an image storing process does not prevent subsequent release of the image upon application of an electric field. Of course, the ability of the phosphor to receive, store, and subsequently release another image is unimpaired.

This invention provides a simple process for storage of an image and subsequent release of the image as visible light upon application of an electric field. An important advantage of the invention is that it permits image storage and release by a phosphor in the presence of electromagnetic radiation of a wave length longer than about 500 millimicrons, including infrared and most of the visible light spectrum. Another advantage is that the stored image can be repetitively produced as visible light by successive applications of electric fields each of a strength or intensity equal to or greater than prior fields. Still another advantage of the invention is that novel storage element is provided which is adapted for image storage and subsequent image release upon application of an electric field. Other advantages will be apparent from the above description of the invention.

The invention claimed is:

1. A tape comprising a layer of a phosphor in a binder, said phosphor comprising a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing manganese in an activating amount of

from about 0.2% to about 2.0% by weight of said metal sulfide.

2. A tape as set forth in claim 1 wherein said binder is a chlorosulfonated addition polymer of an olefin containing 1 to 2 olefinic bonds and not more than 5 carbon atoms.

3. A tape as set forth in claim 1 wherein said layer is coated on a thin flexible support.

4. A tape as set forth in claim 3 wherein said flexible support is polyethylene terephthalate.

5. A tape as set forth in claim 1 which also comprises a selective radiation transmissive material.

6. A tape as set forth in claim 5, wherein said material is a filter dye which is absorbtive of blue and ultraviolet light and is transmissive of electromagnetic radiation of wave lengths longer than 500 millimicrons, X-rays and gamma rays.

7. A process comprising subjecting a phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing manganese in an activating amount of from about 0.2% to about 2.0% by weight of said metal sulfide, to excitation radiation while within an electric field of a strength of less than about 50,000 volts per centimeter, and after cessation of said excitation radiation subsequently subjecting said phosphor to an electric field of strength at least as great as that of the first-mentioned field, wherein said phosphor is exposed to electromagnetic radiation of a wave length longer than about 500 millimicrons between the exposure to excitation radiation and the subsequent exposure to an electric field.

8. The process as set forth in claim 7 wherein said electromagnetic radiation is infrared.

9. A process comprising subjecting a phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zince cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing manganese in an amount of from about 0.2% to about 2.0% by weight of said metal sulfide, to excitation radiation while within an electric field of a strength of less than about 50,000 volts per centimeter, and after cessation of said excitation radiation subsequently subjecting said phosphor to at least one of a mulitple of successive electric fields, each of said fields being of a strength at least as great as any preceding field, said phosphor being exposed to electromagnetic radiation of a wave length longer than about 500 millimicrons between the exposure to excitation radiation and the subsequent exposure to an electric field.

10. A process comprising subjecting a phosphor which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing manganese in an activating amount of from about 0.2% to about 2.0% by weight of said metal sulfide, through a glue-absorbing and ultraviolet absorbing X-ray transmissive filter dye, said dye being in the same binder as the phosphor material, to X-ray excitation radiation transmitted by said filter element, and after cessation of said X-ray excitation radiation subsequently subjecting said phosphor to an electric field, said phosphor being exposed to electromagnetic radiation of a wave length longer than about 500 millimicrons between the exposure to excitation radiation and the subsequent exposure to an electric field.

11. A process for image imposition, retention and release by an excitation-radiation-sensitive phosphor comprising irradiating a selected portion of a layer containing a crystalline luminescent phosphor, which comprises a metal sulfide from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said phosphor containing manganese in an activating amount of from about 0.2% to about 2.0% by weight of said metal sulfide, with an excitation stimulus whereby said phosphor exhibits emission of visible light, said irradiating taking place in the presence of an electric field of a strength of less than about 50,000 volts per centimeter, and, after said irradiating and after said emission of visible light has essentially ceased, subjecting said phosphor to an electric field of a strength at least as great as the first-mentioned field whereby said selected portion exhibits emission of visible yellow-orange light, wherein said phosphor during image retention is exposed to electromagnetic radiation of wave length longer than about 500 millimicrons.

12. A storage element comprising a luminescent material which comprises a metal sulfide taken from the group consisting of zinc sulfide and zinc cadmium sulfide containing up to about 7 mol percent cadmium based on the total amount of zinc and cadmium present, said luminescent material containing manganese in an activating amount of about 0.2% to about 2.0% by weight of said metal sulfide and being characterized by meeting the requirements of the following test: namely, that after subjection of the luminescent material to excitation radiation while the luminescent material is within an electric field of a strength of less than about 50,000 volts per centimeter and upon subsequent subjection, after cessation of said excitation radiation, to an electric field of strength at least as great as that of the first-mentioned field, said luminescent material exhibits an emission of visible light, wherein said phosphor is exposed to electromagnetic radiation of a wave length longer than about 500 millimicrons between the exposure to excitation radiation and the subsequent exposure to an electric field.

13. A storage element as set forth in claim 12 wherein said element also comprises a selective radiation transmissive material.

14. A storage element as set forth in claim 13 wherein said selective radiation transmissive material is a filter dye which is absorptive of blue and ultraviolet light and is transmissive of electromagnetic radiation of wave lengths longer than 500 millimicrons, X-rays and gamma rays.

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