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ELECTRON BEAM RECORDING AND READOUT PROCESS FOR INFORMATION STORAGE AND RETRIEVAL

Filed March 18, 1964

FIG. 1

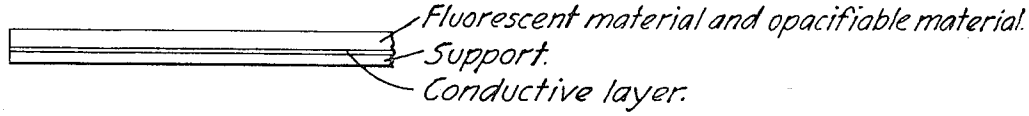


FIG. 2

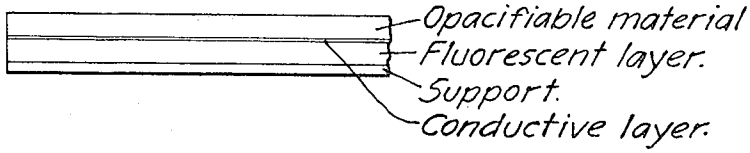


FIG. 3

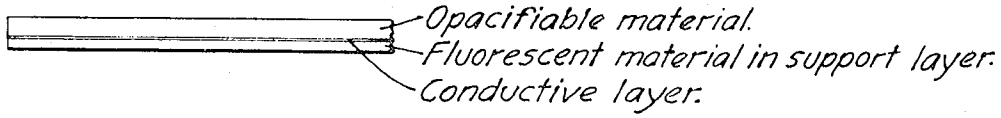
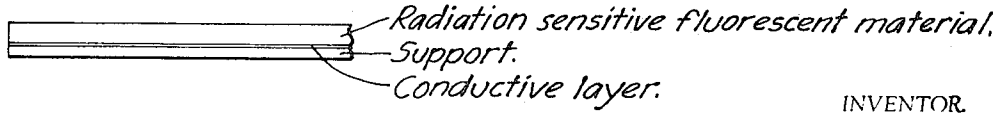


FIG. 4



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ELECTRON BEAM RECORDING AND READOUT PROCESS FOR INFORMATION STORAGE AND RETRIEVAL

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U.S. Cl. 340—173 6 Claims

ABSTRACT OF THE DISCLOSURE

An information storage and retrieval process is shown which utilizes a sheet-like storage member formed of a layer capable of photon emission when uniformly irradiated with an unmodulated electron beam and a layer which is initially capable of chemically and internally selectively altering its initial composition to form a photon masking material upon exposure to differential irradiation wherein the process includes the steps of differentially irradiating the sheet-like storage member whereby the photon transmission properties of the storage medium are selectively altered by the differential irradiation and subsequently exposing the storage medium to electron irradiation so as to produce differential photon emission from the storage medium.

This invention relates to a process for information storage, and retrieval using an electron beam.

The use of an electron beam for recording information has been described in such references as British patent specification 850,985, U.S. Patent No. 3,099,710 and U.S. Patent No. 3,054,961.

The present invention, however, provides an improved information storage and retrieval process whereby to achieve information storage a surface of a storage medium is differentially irradiated by some form of radiation. This differential irradiation represents the information to be stored and retrieved. Thereafter, to achieve information retrieval, a surface of such irradiated storage medium is exposed to uniform electron excitation to produce a differential photon emissive output from the originally differentially irradiated surface of such medium. This photon output is representative of the original differential irradiation.

In general, a storage medium useful in the process of this invention is sheet-like and initially has both:

(a) The capacity to emit photons uniformly from a surface thereof in response to uniform electron excitation of a surface thereof, and

(b) The capacity to alter selectively, chemically and internally its initial composition adjacent a surface thereof in response to exposure of that surface to differential irradiation, so that, either directly or as a result of subsequent processing (i.e. chemical and/or physical treatment) of such medium, such medium thereafter differentially radiates (i.e., transmits, absorbs and/or emits) photon energy in a manner representative of the initial pattern of differential irradiation.

MEDIA AND METHODS FOR MAKING

In general, sheet-like storage media useful in the processes of this invention can be constructed in either of two ways. In one type of construction a storage medium contains both (a) photon emitting electron excitable material, and (b) substances which form a photon masking material upon exposure to radiation. In the second type of construction a storage medium contains materials which are photon emitting in response to electron excitation and, at least initially, so responsive to differential

radiation as to selectively alter their photon emission capabilities (i.e., as by destruction or quenching of photon emission ability) in response to differential radiation above threshold levels. Preferred storage media for purposes of this invention comprise the first indicated type of construction.

In the storage medium construction of FIGURE 1, the photon-emitting, electron-excitable material (herein sometimes called the fluorescent material for brevity) and the substance which forms a photon masking material upon exposure to radiation (herein sometimes called the opacifiable material for brevity) are both dispersed in a suitable light transmissive binder, thus forming a single layer or film in which the fluorescent material is completely embedded, normally on a suitable backing or support member if the single layer or film is not sufficiently self-supporting. The exposed surface is therefore a continuous film of opacifiable material.

Another form of storage medium is shown in FIGURE 3. Here the fluorescent material is uniformly dispersed in a support layer and overcoated on one or both sides with a layer of the opacifiable material.

A more preferred form of storage medium is shown in FIGURE 2 and comprises a sheet-like support, a uniform layer of fluorescent material, and a uniform layer of an opacifiable material.

An additional storage medium, as illustrated in FIGURE 4, consists of a uniform photon emitting layer which is responsive to radiation to alter its photon emission properties, and a sheet-like support.

As illustrated in the storage media embodiments of FIGURES 1–4, it is preferred to use storage media having incorporated therein a layer of an electrically conductive material. By conductive material reference is had to substances such as aluminum, copper, silver, carbon particles, etc., which when in the form of a continuous film, or particulate layer, conduct electrons. A layer of conductive material is so associated with the layer of fluorescent material as to be able to drain off electrons when grounded and thereby provide minimum electrical differential between a medium and the environment. In some media constructions, the conductive layer may be light (photon) transmissive.

In practicing the preferred processes of this invention, one can employ any photon-emitting, electron-excitable material which, when excited by impact of excited electrons, emits photons.

As those skilled in the art will appreciate, fluorescent materials are generally very well known. These conventionally and for purposes of this invention may be finely divided, particulate materials which can be dispersed or suspended in an appropriate solvent binder, or other carrier. Other fluorescent materials are soluble and can be conventionally prepared to give particle- or grain-free layers in storage media. Among these latter substances are the fluorescent dyes and other well known organic fluorescent materials. It will be appreciated that the characteristic wavelengths of the emitted photon radiation may vary from one fluorescent material to another extending from the ultraviolet portion of the spectrum through the visible and into the infrared so that for best utilization of fluorescent materials in the processes of this invention an appropriate matching of the wavelength of the emitted radiation with the spectral sensitivity of the radiation detector is desirable and preferred.

Certain classes of fluorescent materials readily alter their photon emitting properties in response to radiation exposure, such as the metal oxides which are readily reduced to the free metal, are particularly useful in the construction of storage media having a uniform layer of a single active material which not only is initially uniformly photon emitting in response to uniform elec-

tron excitation but which also is selectively responsive to differential irradiation patterns (which results in selective alteration of photon emission properties; see the media construction of FIGURE 4).

It is also possible by combination of fluorescent material with an appropriate radiation sensitive material to form upon exposure to radiation a reactive combination which produces a non-fluorescent reaction product in the irradiated areas.

Similarly one can employ as the substance which forms a photon-masking material upon exposure to radiation any such substance which internally so alters its chemical and/or physical structure in response to radiation exposure of relatively low energy, that a permanent change in its photon-masking properties results. By the term "radiation" reference is had to any of the electromagnetic wave forms commonly classified according to frequency such as Hertzian, infrared, visible (light), ultraviolet, X-ray. Included also are corpuscular emissions such as beta (electrons) radiation, or rays of mixed types. By the term "photon-masking" reference is had to a capacity to mask, as by photon absorption or transmission at one location relative to another in the same material, in response to radiation. Such substances generally are well known. Some opacifiable materials are photon-masking substantially immediately after radiation exposure. Other opacifiable materials require a subsequent development process to effect desired photon-masking. Suitable opacifiable materials include, for example, photographic emulsions (subsequently developed by known photographic development techniques), thermographic systems (which darken upon heating), photoinitiated dehydrohalogenation systems (which darken on heating), diazonium salt-coupler systems (developed by treatment with ammonia vapor or other alkaline substances) and other chemical systems which exhibit selective transparentization and photon-masking in response to differential irradiation.

Certain opacifiable materials such as photographic silver halide emulsions, which exhibit photon-masking in direct proportion to the intensity of the impinging, intensity-modulated radiation beam can be used to provide continuous tone photon masks.

One useful opacifiable material utilizes selective dehydrohalogenation of halogen containing polymers, for example, polyvinyl chloride. In such media, it is the radiation exposed areas which are photon masked upon subsequent heating following irradiation. In general, these systems contain Friedel-Crafts type catalysts which cause the dehydrohalogenation to proceed at a faster rate. Exposing the chlorine containing polymer to actinic light in the presence of the Friedel-Crafts catalyst or Friedel-Crafts cation progenitor and subsequent heating causes the exposed areas to darken more rapidly than the non-exposed areas, thereby producing a negative print. Such processes are described for example in U.S. Patents Nos. 2,712,996, 2,772,158, 2,772,159, 2,754,210, 2,789,053, 2,905,554, 2,905,555, and 2,905,556.

In practicing the invention with a fluorescent recording medium of the type illustrated in FIGURE 4, one should select fluorescent materials which, in addition to the general requirements described above, are known to be sufficiently sensitive to the impinging beam energy provided by practical electron optical systems within relatively short exposure times of about one second or less. Among known materials so sensitive are metal oxides such as indium oxide or zinc oxide or organic fluorescent substances such as 1-phenyl, 2-(p-dimethylaminobenzoyl)-ethylene.

Owing to the fact that the opacifiable material, the fluorescent material, and the conductive material (if present) are each initially present in some form of continuous, thin layer of poor tensile strength characteristics, it is convenient to equip a sheet-like storage medium of this invention with a backing layer or supporting layer so that an entire storage medium in any given construction can be handled, stored, etc., with ease, as those skilled in the art will readily appreciate. In fact, I prefer to practice this invention using supported media. Suitable materials for support layers in storage media include glass, wood, metal (e.g., aluminum foil), paper, cloth, cellulose esters (e.g., cellulose acetate, cellulose propionate, cellulose butyrate, etc.), polyesters, polystyrene, and other plastic compositions. Those skilled in the art will appreciate that a support layer may have in or on its surface suitable conventional materials or substrata needed to facilitate anchorage of the other layers, e.g., of fluorescent material thereon.

When preparing media using both a fluorescent material and an opacifiable material, preferably the total thickness of fluorescent material and of opacifiable material (whether or not the two are separately laid down on the backing as discrete layers or are mixed together as one layer) is kept as thin as possible consistent with the manner in which the invention is to be practiced in any given instance. Also, preferably media include a continuous deposit usually in the form of a separate layer of electronically conductive material therewithin which, when provided with external grounding means, is adapted to bleed off electrons from media, as indicated above.

While no critical dimensions are associated generally with storage media useful in practicing this invention, it will be appreciated that it is usually necessary to design a storage medium to meet the particular conditions of recording and readout arising in the practice of this invention in any particular set of process parameters. Thus, a given storage medium used in any particular process situation should have sufficient respective quantities of, and/or sufficient respective thickness of, fluorescent material, opacifiable material (if used in a given media construction) and (optionally) conductive material to make both recording and readout possible in that particular situation in which such medium is to be employed. Since media constructions can vary widely, no specific size, thickness, composition etc. specifications can be stated that will be applicable or even optimum for all possible use situations. A medium is always constructed so that when after recording or storage, the fluorescent material in the medium is excited to luminescence by energized electrons, there results the desired differential output of photon energy from one surface of said medium uniquely corresponding to the original radiation image or pattern.

PROCESS DESCRIPTION

In practicing the process of this invention using such a medium one first differentially irradiates one surface thereof to store information carried by such radiation in the medium. Thereafter, one illuminates so-irradiated medium with an unmoldulated electron beam to produce a differential photon energy output from one surface thereof, the special distribution of said energy output being representative of the original differential radiation.

(A) *Storing information.*—In storing information by the processes of this invention, it is necessary to modulate the particular form of radiation to be used for storing so as to have the capacity to differentially or selectively irradiate a surface of a storage medium. Modulation can be effected by any conventional process whereby some characteristic of radiation to be used for storage of information in accordance with the teachings of this invention is varied in such a manner or to such a degree that the resulting differential radiation is capable of producing photon masking in the opacifiable material.

For example, storing can involve optical techniques and the use of light images. Thus, a suitable storage medium construction for optical storing techniques can employ a silver halide emulsion layer overcoated with a layer of fluorescent material. The backing can be a polyester film with or without a conductive layer such as aluminum vapor, coated either between the fluorescent layer and the polyester film or between the silver halide emulsion layer and the fluorescent layer. The storage medium can be

made up into a film strip such as a standard 16 mm. film tape and fitted into a conventional 16 mm. movie camera. By appropriate selection of a silver halide emulsion, one can photograph optical images by conventional picture taking techniques with such camera and film. Thereafter, upon conventional silver halide development, one has a storage medium useful within the teachings of this invention from which information stored can be retrieved as hereinafter described.

It will be appreciated that in some types of storing it is necessary to position the recording medium and the apparatus used for generating the differential irradiation in a vacuum chamber, such as is the case, for example, when one records using an intensity modulated scanning electron beam where vacuums of the order of from about 10^{-4} to 10^{-9} mm. Hg are employed, as those familiar with conventional electron beam techniques will readily appreciate. Technology for producing electron beams is well known.

The type of information stored can vary widely. Thus, for example, video signals and facsimile signals can be recorded. In general, the processes of this invention are not limited by the nature of the information to be stored.

During a storing or recording operation, in accordance with this invention, the irradiating with a differential radiation pattern of a surface of a storage medium results in chemically and internally selectively altering the initial composition of such medium adjacent at least one surface thereof. Such alteration results in the creation of a masking layer which is capable of differentially controlling the passage of photon energy therethrough in a manner representative of the initial pattern of differential irradiation.

(B) *Development.*—If following a recording or storing operation the particular storage medium used is one which does not form therein a layer which differentially passes or masks photon energy in a manner representative of the initial pattern of differential irradiation and instead is one which requires subsequent chemical and/or physical treatment to develop a masking layer in which there is an image-wise recording of the initial differential radiation, then such medium must be subjected to an intermediate development step to produce such masking layer. In general, such a development step can involve either solely physical treatment (such as heat, light, pressure, or the like) or some sort of chemical treatment, such as immersion of the medium in a series of solutions; for example, the type of development experienced in the fixing of a silver halide image in a conventional photographic emulsion. Occasionally, some sort of combination of chemical and physical treatment is necessary or desirable.

Since development, if necessary, is entirely dependent on the nature of any opacifiable material used, and since such development involves conventional technology that is not a point of novelty in the present invention, the present specification is not burdened with a needless detailed description of development processes. In general, one simply follows the teachings of the prior art with respect to developmental procedures for producing the desired imagewise mask in or from the original opacifiable material in a particular storage medium. Naturally the medium construction itself is such as to be suitable for any necessary subsequent development following a recording operation.

(C) *Retrieval.*—In general, retrieval is accomplished using uniform electron excitation of the previously irradiated storage medium. Thus, after storage and development (if necessary or desirable) a storage medium is placed in a vacuum chamber and one surface thereof is exposed to a field of excited electrons (e.g. an electron beam as those generated by an electron gun).

When a medium bearing stored information is subsequently excited with an unmodulated electron beam, the fluorescent material is caused to emit photon energy. As this photon energy passes through the photon masking layer, there results a difference in energy emission from the storage medium surface between the differentially masked and unmasked areas. This difference in photon energy emission is detected visually, photo-electronically, by a second photon-sensitive storage media, or by some other form of photon energy detector. Photon energy detectors are well known and include such devices as the eye, cameras, photocells, and the like.

Thus, when such storage medium bearing stored information is subsequently irradiated with energized electrons, as, for example, by an unmodulated electron beam and the medium is excited to phosphorescence, there results in a differentially photon-emissive pattern from the surface of the medium. Electron beams can be conveniently employed to flood the surface of a storage medium with energized electrons.

Usually it is desirable to employ an electron optical system with an electron gun to produce electron beams for retrieval in accordance with this invention. Any conventional electron optical system equipped for producing the desired concentration of accelerated electrons over the specified retrieval area can be utilized. In certain instances the accelerated electrons may be focused into a small beam which can be scanned over a target field used for readout in accordance with the teachings of this invention. The beam generated is not modulated. Retrieval (readout) is often conveniently achieved merely by a visual inspection of the recorded surface. Sometimes a conventional optical system is desirable in order to magnify the photon-emissive surface of a prerecorded medium by a readout with a scanning unmodulated electron beam.

The following examples illustrate further the processes of this invention:

Example 1

A two mil wet coating of the following homogeneous formulation is coated onto a 0.75 mil aluminum foil substrate and then dried:

	Grams
Zinc oxide (fluorescent material)	2.0
Opacifiable material:	
Copolymer of 87 mol percent Vinyl chloride and 13 mol percent Vinyl acetate	2.0
Acetone	8.0

Using the resulting storage medium, recording (storing) is effected in each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam with, for example, the characteristics of 20 kilovolts, 5 microampere peak target current in a 0.5 x 10^{-3} inch beam spot, scanning out a 0.5 x 0.5 inch raster for times ranging from $\frac{1}{30}$ to 3 seconds.

(b) A sample is flooded with a non-scanning beam through an image-wise mask of total dimensions 0.5 x 0.5 inch with a 20 kilovolt, 5 microampere unmodulated electron beam for times ranging from $\frac{1}{30}$ to 3 seconds.

(c) A sample is exposed for 5 seconds to ultraviolet light by placing it 10 inches from an ultraviolet lamp having the trade designation B–H6 as sold by the General Electric Co.

Thereafter, each sample is heated to 150° C. until a black color is formed selectively in the irradiated area. The recorded information is observed in each of two ways, first by scanning and then by flooding each sample in vacuo with 10 kilovolt electrons providing an image-wise differential fluorescence by exciting fluorescence of the zinc oxide in the unirradiated areas, the image areas being effectively masked.

Example 2

Aluminum foil is coated with a 2 to 3 mil (wet coating thickness) layer of a ball milled mixture of very finely powdered zinc oxide (the fluorescent material), 10 grams of a butadiene and styrene copolymer (30/70 mil ratio respectively) and 50 grams of toluene. After the coating is dry, the resulting film is further coated at a wet thickness of 2 mils with a coating composition containing

10 grams resorcinol, 0.5 gram of the zinc chloride double salt of p-diethylaminobenzenediazonium chloride and 4.0 grams of a polyamide ("Zytel," a trademark of the Du Pont Co. of its brand of polyamide resin) binder in 16 grams methanol (the opacifiable material). The resulting yellowish sheet is dried in a dark room.

Using such sheet recording is effected by each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam of 20 kilovolts and 5 microampere peak target current in a 0.5 x 10^{-3} inch beam spot which scans out a 0.5 x 0.5 inch raster for times ranging from $\frac{1}{30}$ to 3 seconds.

(b) A sample is flooded with a non-scanning beam through an image-wise mask of total dimensions 0.5 x 0.5 inch with a 20 kilovolt, 5 microampere unmodulated electron beam for times ranging from $\frac{1}{30}$ to 3 seconds.

(c) A sample is exposed for 5 seconds to ultraviolet light by placing it 10 inches from an ultraviolet lamp having the trade designation B–H6 as sold by the General Electric Co.

Thereafter, each sample is developed with ammonia vapor which produces a yellow-brown coloration in the unexposed areas and translucent images in the exposed areas corresponding the recorded information.

The recorded information is observed in each of two ways, first by scanning and then by flooding each sample in vacuo with 20 kilovolt electrons, producing an image-wise differential fluorescence by exciting fluorescence of the zinc oxide in the image areas, the background areas being effectively masked.

Example 3

Aluminum vapor coated polyethylene terephthalate film is coated with a 2 to 3 mil (wet coating thickness) layer of a ball milled mixture of very finely divided zinc oxide (the fluorescent material), 10 grams of butadiene-styrene copolymer (30/70 mil ratio respectively) and 50 grams of toluene. A suspension of 6 parts by weight of an equal mole percent mixture of silver behenate and behenic acid is dispersed in a solution of 1.5 parts of polystyrene resin in a mixture of 16 parts heptane and 26.5 parts acetone by ball milling to a smooth dispersion. Separately, 1.5 parts of methyl gallate, 0.1 part of 2,3-dihydroxybenzoic acid and 0.2 part of phthalic anhydride are stirred into a solution of 11.6 parts of polystyrene resin in 13.6 parts heptane and 23 parts acetone. The two solutions are blended together and the blend coated smoothly on the coated aluminum foil sheet, this second coating (the opacifiable material) weighing about 0.5 gram per square foot, equivalent to about 21 milligrams of silver.

Using the resulting storage medium, recording is effected in each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam of 20 kilovolts and 10 microampere peak target current in a 0.5 x 10^{-3} inch beam spot which scans out a 0.5 x 0.5 inch raster for times ranging from $\frac{1}{30}$ to 3 seconds.

(b) A sample is flooded with a non-scanning beam through an image-wise mask of total dimension 0.5 x 0.5 inch with a 20 kilovolt, 5 microampere unmodulated electron beam for times ranging from $\frac{1}{30}$ to 3 seconds. No image is visible until the sample is heated for several seconds following exposure. A black silver image is then formed in the irradiated areas due to the further reduction of free silver by the reducing agents in the presence of heat.

When each so-recorded sheet is scanned or flooded in vacuo with the same (unmodulated) electron beam, the recorded information is observed by fluorescence of the zinc oxide in the background areas of the sample sheet; the image areas are effectively masked.

Example 4

A 5-mil polyethylene terephthalate sheet is vapor coated with aluminum, the resistance of which is 0.4 ohm per square (about 2000 angstroms thickness). The aluminum vapor coating is then coated with a composition containing 200 grams of zinc oxide, 50 grams of butadiene-styrene binder and 450 grams of a 1:1 weight ratio mixture of acetone and toluene, the resulting coating being about 15 microns thick. A further coating (about 3 microns dry thickness) is then provided, using a photosensitive emulsion (19% solids) having 12 weight percent gelatine, 7 weight percent silver halide (80/20 ratio of silver chloride/silver bromide) and wetting agents.

Using the so-prepared storage medium, recording is effected in each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam at 10 kilovolts and 0.1 microampere peak target current in a 0.5 x 10^{-3} inch beam spot scanning out a 0.5 x 0.5 inch raster in $\frac{1}{60}$ second.

(b) A sample is flooded with a non-scanning electron beam through an image containing mask of dimensions 0.5 x 0.5 inch with a 10 kilovolt, 0.1 microampere unmodulated beam for $\frac{1}{60}$ second.

(c) A sample is illuminated with visible light via conventional camera means.

In each instance, the result is a latent, photographic image formed in a surface of each sample which is developed by usual photographic development and fixing. A black silver image is formed in the beam- or light-struck areas. Upon exposure in vacuo of each so developed sample first to an unmodulated scanning beam and then to a flooding 20 kilovolt electron beam for readout, the beam excites fluorescence of the zinc oxide in the background areas, and the recorded information is observed; the image areas are effectively masked.

Similar results are achieved when a soluble organic dye or scintillator dissolved in a suitable plastic is used in place of the zinc oxide layer.

Example 5

A 0.15 mil polyethylene terephthalate film is vapor coated with an electrically conductive layer of aluminum so that the film is 50% transparent to light. On the aluminum side is knife coated a 20% by weight polymer solution of polymethylmethacrylate in tetrahydrofuran containing 20 mg. of technical anthracene per ml. of solution such that on drying the film has a thickness of 0.5 mil and shows a yellow fluorescence upon stimulation by 2537° ultraviolet light (the fluorescent layer).

Over this dry film is knife coated a 20% by weight polymer solution of an 87:13 copolymer of vinyl chloride: vinyl acetate in methylethyl ketone containing 20 mg. of the acid sensitive dye p-aminoazobenzene per ml. of solution such that on drying this film has a thickness of 0.1 mil (the opacifiable layer).

Using the so-prepared storage medium, recording is effected by each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam of 20 kilovolts and 5 microampere peak target current in a 0.5 x 10^{-3} inch beam spot which scans out a 0.5 x 0.5 inch raster for times ranging from $\frac{1}{30}$ to 3 seconds.

(b) A sample is flooded with a non-scanning beam through an image-wise mask of total dimensions 0.5 x 0.5 inch with a 20 kilovolt, 5 microampere unmodulated electron beam for times ranging from $\frac{1}{30}$ to 3 seconds.

(c) A sample is exposed for 3 seconds to ultraviolet light by placing it 10 inches from an ultraviolet lamp having the trade designation B–H6 as sold by the General Electric Co.

The above-mentioned radiation striking the polymer-p-amino-azobenzene layer produces a red color. Upon exposure of each sample in vacuo to a scanning or to a

flooding 20 kv. electron beam, the recorded information is observed by the differential photon emission produced.

Example 6

Aluminum foil is coated with a 2 mil wet coating of a 10% solution (based on the weight of polymethylmethacrylate) of 1 - phenyl,2 - (para - dimethylaminobenzoyl)-ethylene in a solution of 20% polymethylmethacrylate in methyl ethyl ketone.

This information is allowed to dry. Using samples of this storage medium recording is effected in each of the following ways:

(a) A sample is scanned in a raster pattern under high vacuum with an intensity modulated electron beam of 20 kilovolts and 5 microampere peak target current in a 0.5 x 10^{-3} inch beam spot which scans out a 0.5 x 0.5 inch raster for times ranging from 1/30 to 3 seconds.

(b) A sample is flooded with a non-scanning beam through an image-wise mask of total dimensions 0.5 x 0.5 inch with a 20 kilovolt, 5 microampere unmodulated electron beam for times ranging from 1/30 to 3 seconds.

(c) A sample is exposed for 5 seconds to ultraviolet light by placing it 10 inches from an ultraviolet lamp having the trade designation B–H6 as sold by the General Electric Co.

In recording cases (a), (b) or (c) above, the fluorescence capability on readout is effectively quenched in the irradiated areas.

To this mixture was then added enough extra solvent to render it of the consistency of heavy cream, this producing a favorable viscosity for pebble milling. The amount of solvent thus added varied from sample to sample, in the range of 5 to 25 additional for 10 grams of pigment, resin, and original solvent.

The mixture was then pebble milled in a 1 oz. vial, containing 1/8 inch pebbles, for 4 hours or until smooth enough for coating. It was then coated on a substrate (column D) to a wet thickness of 0.5 mil, dried, and mounted in the vacuum system for test.

Test recording was by means of a TV raster pattern in a 10^{-3} mm. Hg vacuum with an intensity modulated electron beam of the voltage and current indicated in columns E and F for the time cited in column G. The spot diameter in these tests was of the order of 50 microns, although this was not a critical factor for showing the recording process.

In some instances the image formed by the recording operation was developed in order to make it stable with respect to subsequent irradiation with an unmodulated electron beam raster during readout, as noted in column H. In these cases the required voltage (column I) could be equal to the recording voltage. In other instances fluorescence was produced by a lower voltage or a shorter time of exposure to the electron beam so that clear readout could be achieved before destruction of the original recorded image occurred by the readout process.

TABLE I

A	B	C	D	E	F	G	H	I	J
Flrscent. material	Binder (solv.)	Layer thickness (mil)	Pigment to binder ratio	Substrate	Kv.	μA.	Frames	Development	Readout voltage for fluor. kv.
HgO	Pliolite S-7 [1] (toluene).	4	6:1	Paper aluminum.[2]	15	35	60	Direct development by EBB.[3]	15
In_2O_3	do	5	4:1	do	15	35	1	Electrolytic reduction.[4]	15
ZnO	do	5	6:1	do	20	10	90	Direct development by EBB.	10
ZnO+Starch [5]	VYHH [6] (methylene chloride).	8	3:1	Polyethylene terephthalate [7] aluminum.	25	200	30	do	10
PP Methylenebis (N, N-dimethylaniliη).	do	4	2:1	Mylar [8]	25	65	1	do	10
In_2O_3	do	0.1	2:1	do	25	160	1	do	10
Dimethoxy ferric formate+ZnO [12]	do	0.1	1:10	Paper aluminum	25	160	1	Heat development. [10]	10
ZnO	do	1.0	5.5:1	MOT paper [11]	25	200	1	do	10
Methyl red+ZnO [9]	do	0.5	4:1	Paper aluminum	25	160	1	Direct development.[13]	10
Methyl yellow+ZnO [14]	VYHH (methylene chloride).	0.5	4:1	do	25	160	1	do	10

[1] Pliolite S-7—The styrene butadiene copolymer sold by the Goodyear Company.

[2] Paper aluminum—The paper aluminum substrate is a laminate made by placing together an aluminum foil of about 0.5 mil in thickness and a bond paper of about 2 mils in thickness under sufficient pressure to effect adherence of the paper to the foil without a binder.

[3] Direct development by EBB—No development.

[4] Electrolytic reduction—Electrolytic reduction is accomplished by the techniques described in U.S. Pat. No. 3,085,051.

[5] ZnO+starch—The weight ratio of zinc oxide to starch is 1:1.

[6] VYHH—A film about 8 mils in thickness sold by the Bakelite Corporation and containing about 87% polyvinyl chloride and about 13% polyvinyl acetate.

[7] Polyethylene terephthalate—The polyethylene terephthalate is about 1.5 mils in thickness.

[8] Mylar—The Mylar is vacuum vapor coated with aluminum. Mylar thickness is about 2.5 mils: the vapor coated aluminum about 0.1 mil.

[9] Dimethoxy ferric formate+ZnO—The weight ratio of dimethoxy ferric formate to zinc oxide is 1:1.

[10] Heat development—Development achieved by using a hot air stream having a temperature up to about 400° C. produced by a hot air gun of the type conventionally used as hand-held hair dryers. The hot air stream is directed against the sample for a time sufficient to develop an image (usually about 30 seconds.)

[11] MOT Paper—A number 25 map overlay tracing paper of the tissue type sold by Rhinelander Paper Company.

[12] Methyl red+zinc oxide—The weight ratio of mehyl red to zinc oxide is 1:5.

[13] Direct development—No development.

[14] Methyl yellow+zinc oxide—The weight ratio of methyl yellow to zinc oxide is 1:5.

The recorded information is observed in vacuo by scanning or by flooding with a 10 kv. electron beam producing a differential fluorescence pattern corresponding to the recorded information.

Examples 7–15

In the following examples, summarized in Table I below, the fluorescent material (column A) was stirred into a solution of binder resin in solvent (column B), the relative amounts of pigment and resin solids being shown (column C). For example, for 6 grams of zinc oxide mixed with 3.33 grams of 30% Pliolite S-7 in toluene, the solids ratio of pigment to binder is 6/1.

Having described my invention, I claim:

1. A process for information storage and retrieval comprising the steps of differentially irradiating a surface of a sheet-like storage medium formed of a layer capable of photon emission when uniformly irradiated by an unmodulated electron beam, a layer initially capable of chemically and internally selectively altering its initial composition adjacent one surface thereof upon exposure of that surface to said differential irradiation and a separate conductive layer for removing electron charges from said medium, thereby selectively changing the photon transmission properties of said storage medium in

those surface areas so selectively altered by said differential irradiation resulting in a differentially photon emitting pattern, and, without further application of a layer capable of photon emission when uniformly irradiated by an unmodulated electron beam, subsequently exposing said storage medium to uniform electron irradiation so as to produce differential photon emission from said differentially photon emitting pattern.

2. A process for information storage and retrieval comprises differentially irradiating the surface of a storage medium containing both a photon emitting material sensitive to an electron bean and a substance which forms a photon masking material upon exposure to said differential irradiation each of which are in separate layers and a conductive layer for removing electron charges from the medium whereby a differentially photon emissive pattern is formed on the radiated surface of said storage medium, and, without further application of photon-emitting material sensitive to an electron beam, subsequently exposing said storage medium to an electron beam to cause photon emission from said photon emitting material and thereby produce a differentially photon emissive pattern from the surface of said storage medium.

3. A process for information storage and retrieval which comprises scanning with an intensity modulated electron beam the surface of a storage medium containing both a photon emitting material sensitive to an electron beam and a material which forms a photon masking material upon exposure to said electron beam whereby a differentially photon emissive pattern is formed on the so-scanned surface of said storage medium each of which is a separate layer and a conductive layer for removing electron charges from said medium, and, without further application of photon-emitting material sensitive to an electron beam, subsequently irradiating again said storage medium with an unmodulated electron beam to cause photon emission from said photon-emitting material and thereby produce a differentially photon emissive pattern from the surface of said storage medium.

4. A process for information storage and retrieval comprising the steps of differentially irradiating a surface of a sheet-like storage medium formed of a layer capable of emitting photons uniformly from a surface thereof in response to uniform electron excitation of a surface thereof, and a layer initially capable of chemically and internally selectively altering its ability to radiate photon energy from one surface thereof upon exposure of that surface to said differential irradiation, thereby effecting selective changing of the photon transmission properties of said storage medium from those surface areas so selectively altered by a said differential irradiation resulting in a differentially photon emitting pattern and a separate conductive layer for removing electron charges from said medium, and, without further application of a layer capable of emitting photons in response to uniform electron excitation, subsequently exposing a surface of said storage medium to uniform electron excitation so as to emit photons uniformly and thereby produce differential photon emission from said initially differentially irradiated surface in a manner representative of said initial differential irradiation.

5. A process for recording and reproducing information comprising the steps of

differentially irradiating and information storage medium formed of a photon emissive layer capable of producing uniform photon emission therefrom when uniformly irradiated with an unmodulated electron beam and a separate photon masking layer capable of being chemically altered upon exposure by differential irradiation whereby the photon transmission characteristics of said photon masking layer are selectively altered by said differential irradiation representing said information to be stored on said medium and a separate conductive layer for removing electron charges from said medium; and, without further application of a photon emissive layer capable of producing uniform photon emission therefrom when uniformly irradiated with an unmodulated electron beam,

reproducing information by uniformly irradiating said storage medium with an unmodulated electron beam whereby said medium produces differential photon emission therefrom representing information stored on said medium.

6. The process of claim 1 wherein said photon emission from said photon-emissive pattern is detected photoelectronically.

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